2012

Impacts Of Land Use/Land Cover and Soil on Water Quality in the Upper Little Miami River Sub-Basin

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IMPACTS OF LAND USE/LAND COVER AND SOIL ON WATER QUALITY IN THE UPPER LITTLE MIAMI RIVER SUB-BASIN

A thesis is submitted in partial fulfillment

of requirements for the degree of

Master of Science

By

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Bangalore, India

2012

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WRIGHT STATE UNIVERSITY

SCHOOL OF GRADUATE STUDIES

April 13, 2012

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Akshaya Kumar Devendra ENTITLED Impacts of land use/land cover and soil on Water Quality in the Upper Little Miami River sub-Basin BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

Devendra, Akshaya. M.S. Department of Earth and Environmental sciences, Wright State University, 2012. 'Impacts of land use/land cover and soil on Water Quality in the Upper Little Miami River sub-Basin'

The Little Miami River Basin (LMRB) is increasingly becoming susceptible to the degradation of water quality due to various factors such as increase in urban landscape and agricultural runoff. This study is about understanding the impact of land use/land cover (LULC) and soil on water quality in LMRB.

It was assumed that the major sources of solutes in the river mainly originated from the leaching of the land by precipitation and the composition of the leachate is influenced by the type LULC and soil. Least square method was modified to estimate the production coefficient for each of the types of LULC and soil properties.

Streams in urban areas clearly carried higher levels of Total Phosphate (TP) at mean concentrations of about 0.56 mg/L. The nitrate levels in the streams near agriculture area was observed in elevated levels with mean concentrations at 3.2 mg/L. Production coefficients for TP and nitrate are (0.036, 0.009) and (0.004 and 0.033) for urban and agriculture land use, respectively. Production coefficients for excessively drained areas on the soil maps were 0.105 mg/L/acreage percent for TP and 0.059 mg/L/acreage percent for N. The streams carrying more amounts TP coincided with excessive drainage, OM and urban areas. But, further analysis showed that TP levels were directly influenced by drainage rather than urban areas or OM.

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ACKNOWLEDGEMENTS

Firstly, I would like to acknowledge Dr. Songlin Cheng, for his patient yet effective way of advising. He has been a constant motivation to me throughout this entire research project. I would like to thank him with immense gratitude, for all the support and guidance he provided to successfully complete this project.

I would like to sincerely thank Dr. Abinash Agrawal from the bottom of my heart for his insights and recommendations as a committee member. As a Graduate studies chair he instilled lot of confidence in me and showed great support throughout. Dr. Doyle Watts, he readily accepted my request to be a part of my committee without any hesitation. I sincerely thank him for his inputs and feedback.

I would like to thank Dr. David Dominic for his belief and support at various times during my entire stay with the department. I have always looked up to him for any help. I am very thankful to the Department of Earth and Environmental sciences for providing me the great opportunity to work as a GTA. It has been a honor to be a part of this department.

I would also like to thank Suzanne, Cindy, Leslie and Mr. Bourne. Also, I would like to thank all other faculty and staff of the department who made my journey a successful one.

To my friend Ashish, for helping collecting samples and Lee Porter, for being such a source of help, I thank you.

Finally to my family, thanks to my brother Dr. Naga Dharshan, In-laws Mr. Jaykumar, Mrs. Kalpana Jaykumar, Rashmi Dharshan, Niki, Nishkru and my family well-wisher Mr. Chenna Murthy, for their support and sacrifices. Last but not least thanks to my lovely wife Nishita, for being kind and supportive even when I was far away from her.

Dedicated to my parents

Sarala Devendra and Devendra Guptha

"*I have little words to say, but way too much to express,*

For all that you sacrificed just to see me grow,

all I can say is,

the glory belongs to you and only you."

- *Akshaya Devendra*

1.0 INTRODUCTION

1.1 Water quality in streams and rivers

Water quality is very important for human health as well as the other living organisms. Water quality of a stream mainly depends on many physiological factors including the climate, land cover of that particular watershed and soil conditions (Tong & Chen, 2002). Due to increasing population and more intense agricultural practices has led to increase in the urbanized areas and large use of fertilizers. Due to urbanization the land cover within river basins has drastically changed and this change has started to have serious effects on the quality of rivers. Runoff from agriculture, effluents from domestic and industrial sources and also from waste water treatment plants have degrading effect on rivers (He et al., 2009). Parameters such as rainfall, runoff from land surface play a vital role in estimating the quality of the river. Anthropogenic sources such as the use of fertilizers in agriculture and effluent discharge run directly or indirectly into the stream (Jarvie et al., 2002). It was found that the agricultural and impervious land surfaces produced the most amounts of nitrate and phosphate when compared to other land surfaces (Tong & Chen, 2002). Also, areas with poultry production produced more nitrate and phosphate in the watershed (Fisher et al., 2000).

Natural sources of nitrogen in watershed are either from lightening-produced or mediated microbially through nitrogen cycle. Precipitation in the watershed also affects the levels of nitrogen in urban streams. It is found that nitrate levels are elevated during the rainy season and lowered in the dry seasons. These levels also depend on seasonal application of manure (Brett et al., 2005). Whereas, natural phosphate levels are regulated by physical processes such as weathering, erosion, transport of the sediment.

One big problem associated with the nutrient discharge from the catchments zones into water bodies is eutrophication. The term eutrophication refers to nutrient enrichment in the water bodies such as rivers and lakes. The excessive nutrient results in algal bloom. As the algae die over the period of time the organic matter as a result consumes dissolved oxygen. Due to the decrease in dissolved oxygen concentrations the organisms living in water cannot sustain its life. The sources of excessive nutrients vary from agriculture runoff or the sewage effluents. Grand lake St. Marys, the largest inland lake in Ohio was the biggest manmade lake in the world when it was built between 1837 and 1845 as feeder for Erie Canal system (Journal Gazette, 2010). This lake is well known for recreational activities, is now on the verge of dying due to restrictions imposed by the EPA. Uncontrolled agricultural fertilizer runoff has led to eutrophication and as a result of this there is a bloom of harmful Algae.

Several studies have stressed on the importance of linking the catchment characteristics with that of the stream water quality (Tong & Chen, 2002; Jarvie et al, 2002; Ahearn et al, 2005; Brett et al, 2005). The linking of catchment characteristics to the stream water quality gives further understanding of the influence of different land use/Land cover(LULC) in the watershed on the water quality (Arheimer, 2000).

Point and Non- point source pollutants are two terms usually associated with water pollution sources. Point sources are a pollution discharged from a source such as waste water treatment plants, factories, feeding operations etc. As per EPA's definition, it is defined "any single identifiable source of pollution from which pollutants are discharged, such as a pipe, ditch, ship or factory smokestack" (NOAA, 1997). On the other hand non-point source pollutants have a very broad sense. It is caused by the runoffs from the rain or snow melt. As the runoff moves along the surface of the ground it carries pollutants such as fertilizer, chemicals, petroleum products found on the ground and drains into the streams.

Riparian zones are a thin line of grass, shrubs or trees along the streams where the water is in touch with the land. These zones are very important for the water quality in the streams and act as buffers. These buffers are very essential because they prevent pollutants such as nutrients, pesticides, sediment etc. in reaching the streams. They also act as a major source of energy to the living communities in the streams by providing food and also act a valuable habitat for variety of animals and birds. Riparian zones helps in slowing down the flood waters thus preventing erosion of the banks and in the process helps the sediments to settle down (Riparian buffers, 2008). Loss or absence of riparian buffers results in erosion, runoff's draining into the streams, loss of habitats and more importantly leads to poor water quality.

Non-point source (NPS) nutrients are difficult to estimate as they are contributed from many different smaller sources and they tend to diffuse in nature. Loss of forest cover and increase in impervious surfaces due to urbanization has an effect on nutrient upload in the streams (Brett et al., 2005). When considering an urban land cover as a non-

point source of nutrient in the streams concentrations were not genuine, as majority of the areas are impervious and the water diverted to sewage treatment plants where it is discharged into the local streams. Hence these streams could carry loads from other basin (Ahearn et al, 2005).

Reports suggest that more than 90% of the rivers and streams in Ohio are impaired and at least 50 % of them are affected due to nutrient uploads (USEPA, 2008). The Little Miami River Basin (LMRB) located on the south western region of Ohio is impacted mainly due to nutrient enrichment and sedimentation among others. According to the report published by the Ohio EPA in 2002, the upper LMRB was listed in the 303(d) list of impaired waters and these waters are troubled both by point and non-point sources of pollution (Ohio EPA, 2002).

1.2 Previous Studies

There are number of studies and mathematical models being used to estimate the amount of nutrient/pollutant load in the streams (Wang & Yin, 1997; Ahearn et al, 2005; Holloway, 2005; France 2005; Chang, 2008). All the previous studies were either used GIS tools such statistical analysis, spatial analysis, remote sensing or used the mathematical models. Some previous studies at Wright State have been done on the impact of land use on water quality. One study by France (2005) used the remote sensing approach to relate the water quality of the Mid-Ohio River watershed with the urban areas with the help of data from STORET, an USEPA's water quality database.

Another study by Holloway in 2005 also made use of remote sensing and STORET to determine how the changes in the land use can temporally vary the stream quality for over a period. Belke (2007) examined the relationship between land use and water quality using an algebraic expression that related the quality of water to that of the land type. In his study he used the GIS modeling with the help of ArcGIS and ArcHydro to delineate the watershed and sub-watersheds. It was time consuming and needed several laborious steps for processing of the data. BASINS was used an alternative for his study since it provided integrated tools for downloading data, delineating watersheds and generate the characterization report for each land type within sub watersheds. As an enhancement to Belke's study for finding production coefficient, in this study zonal statistics were used to estimate the percentage of each LULC class in the catchment.

1.3 Assumption

The major sources of solutes in the river mainly originated from the leaching of the land by precipitation. The composition of the leachate is expected to be influenced by the type of Land use/Land cover (LULC). Assuming uniform amount of precipitation over a catchment, the relative size of each LULC should dictate its extent of influence on solute concentration in river. The catchment size should not be the major factor, since the amount of precipitation will increase proportionally. If so, the solute concentration at the outlet of the catchment should be a mixture of leachates from each LULC category and can be evaluated by

$$C_i = \sum_{i=1}^{N} A_i . P_i \qquad \text{Eq. 1}$$

Where,

C_i is concentrations of solutes at catchment outlet,

A_i's are the percent size of LULC in a catchment, and

P_i's are the production coefficients, which have a unit of mg/l per percent of area of LULC category. It represents a contribution fraction of solute from each LULC category.

The contribution from ground water is not explicitly included in the calculation. However, groundwater is essentially precipitation percolating through the land surface, and therefore the chemical composition of groundwater should reflect the LULC and soil.

Therefore, ground water component in the river water implicitly reflects the impact of LULC and soil, and the proposed equation is still reasonable.

1.4 Purpose of the study

In order to relate the non-point sources of pollutants and their loading in the rivers, a relationship between streams and land use characteristics needs to be established. This understanding can help in the betterment of watershed management to improve water quality.

This study deals with nutrients, silica, and other solutes in the upper LMRsB and the effect of drainage characteristics on their concentrations in the streams.

The main purpose of this project is to quantify the impact of LULC and soil on stream water quality by the above method using GIS maps with land use, hydrology, soils, and other characteristics of the basin. In addition, I will also investigate what hydrogeochemical processes influence the major water chemistry in this watershed.

2.0 THE STUDY SITE

2.1 Little Miami River sub-Basin (LMRB, HUC 05090202)

2.1.1 Physical description

Little Miami River is a 170-km long tributary of the Ohio River that drains a 4,535 km^2 river basin in the south western Ohio (Figure 2.1). The source of the main stream is just few miles south-east of Springfield and the length of the stream is less than 160 km.

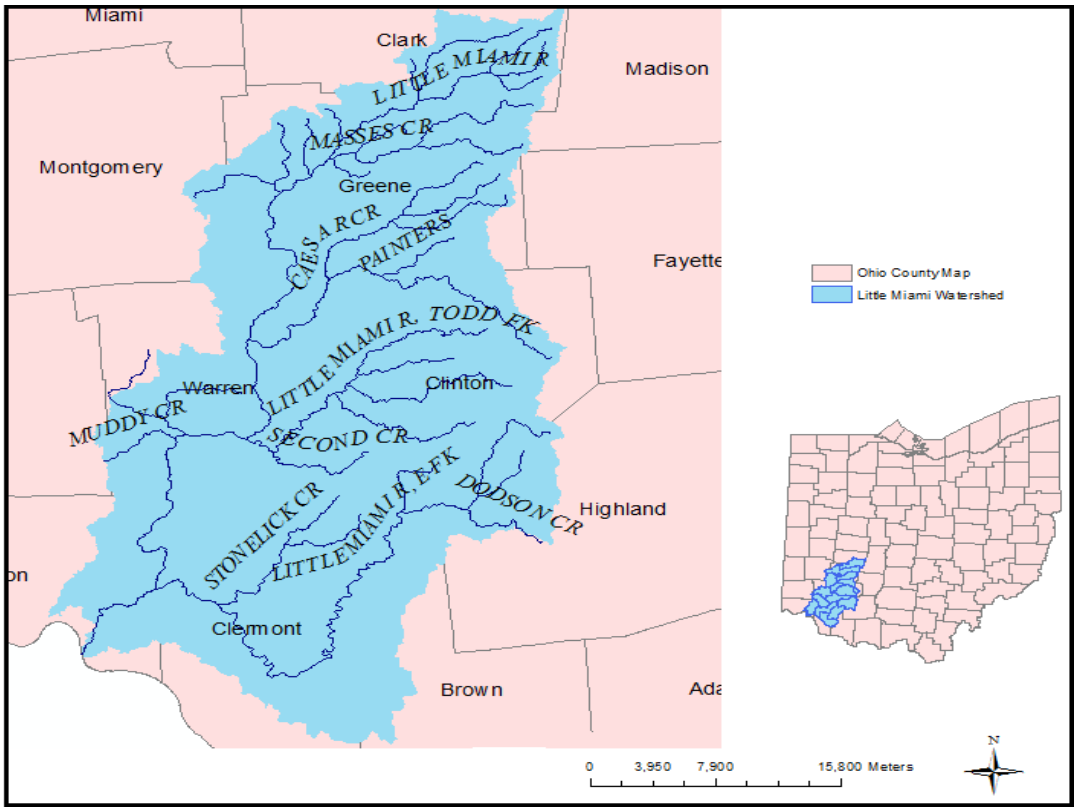


Figure 2.1 Little Miami River Basin, Ohio

East fork is the main tributary of this river. Other tributaries include Sugar Creek, North Fork, Todd's Fork, Duck Creek, Caesar Creek, Massie Creek, and Turtle Creek. The Basin covers portions of 6 counties including Clark, Madison, Greene, Montgomery, Warren and Clinton (Ohio EPA, 2002). The river drains into the Ohio River near Cincinnati.

The northern portion of the river has gently rolling plains with low gradient tributaries due to Wisconsinan glaciation and southern half of the river has low and medium gradient tributaries. The till plain soils from Wisconsinan glacier tills and outwash are more permeable soil and less erodible soils as compared to older soils of the drift plains (Daniel et al., 2010). This river is a designated State and National Scenic River, with scenic and most diverse habitats.

2.1.2 Geology

The bedrock of this basin is mainly dominated by Pleistocene calcareous shale, dolomite and limestone of Ordovician and Silurian age. Glacial till is the major surface component of the LMR basin. The large streams are underlain by the buried valley aquifer mostly composed of highly permeable sand and gravel. Since this aquifer is the major source of drinking water, the USEPA has termed it as a sole source aquifer (Ohio EPA, 2002).

2.2 Study Area

Northern portion of the Little Miami River Basin, including the tributaries such as North fork little Miami, Massies creek, Beaver creek, is the focus of this study. The study area is approximately 773 sq. km and covers portions of Clark, Greene and Montgomery counties. Land use in this region is primarily agriculture, except the Dayton-Xenia corridor, that includes the city of Beavercreek, which is predominantly urbanized. The study area was divided into 6 catchment areas which are drained by various tributaries of LMR as seen on Figure 2.2

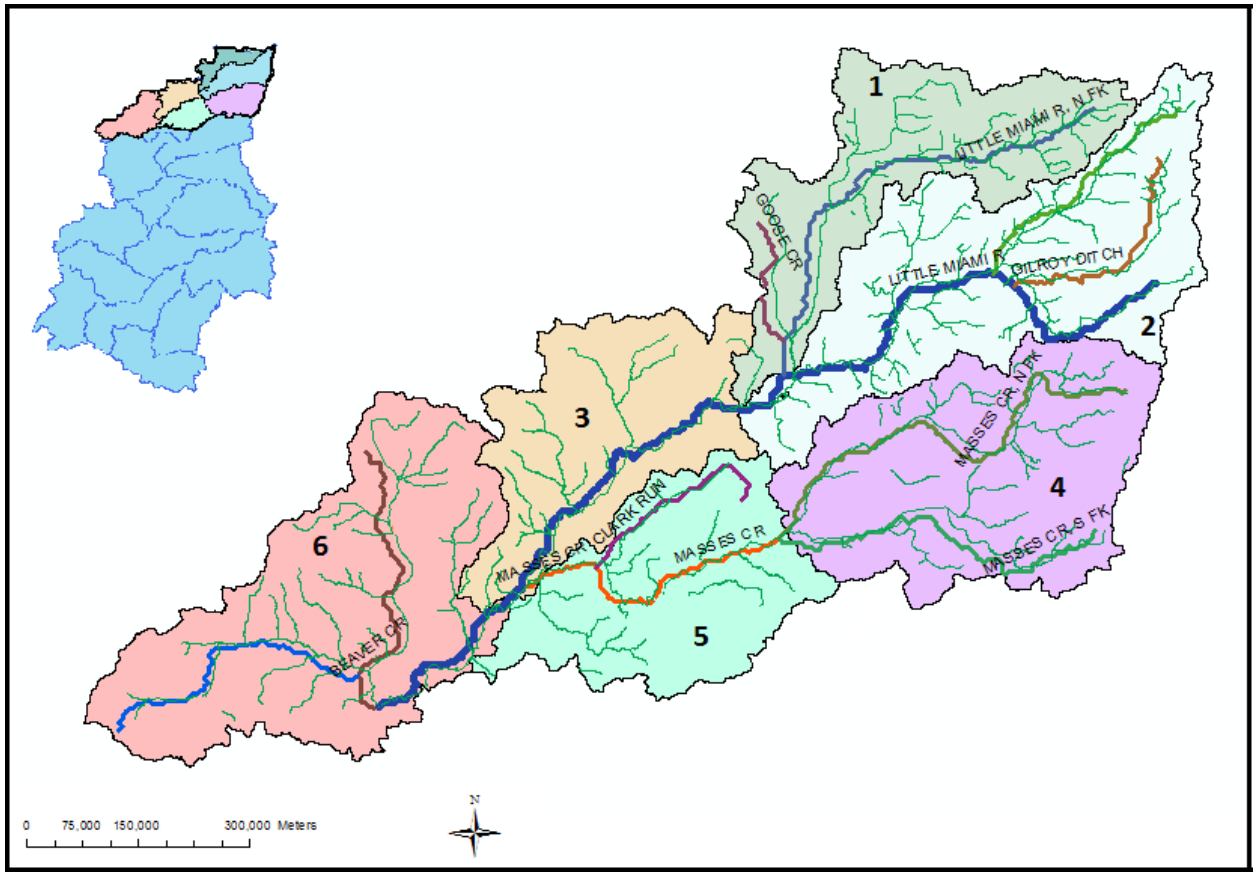


Figure 2.2 Map of the upper LMR sub-Basin used for study.

2.4 LULC of the study area

The Figure 2.3 shows the LULC distribution in the study area. Table 2.1 gives the percentage of area of various land use/land cover types of the study area. The major type of land use is agriculture at about 86 %. Hence, agriculture runoff can significantly affect the water quality of the streams. The urban area group that includes residential and industrial comprises about 12% of the study site. Seventeen water bodies within the upper little Miami watershed featured in1998 CWA 303(d) list as impaired due to Nutrient a degraded habitats (Ohio EPA, 2002).

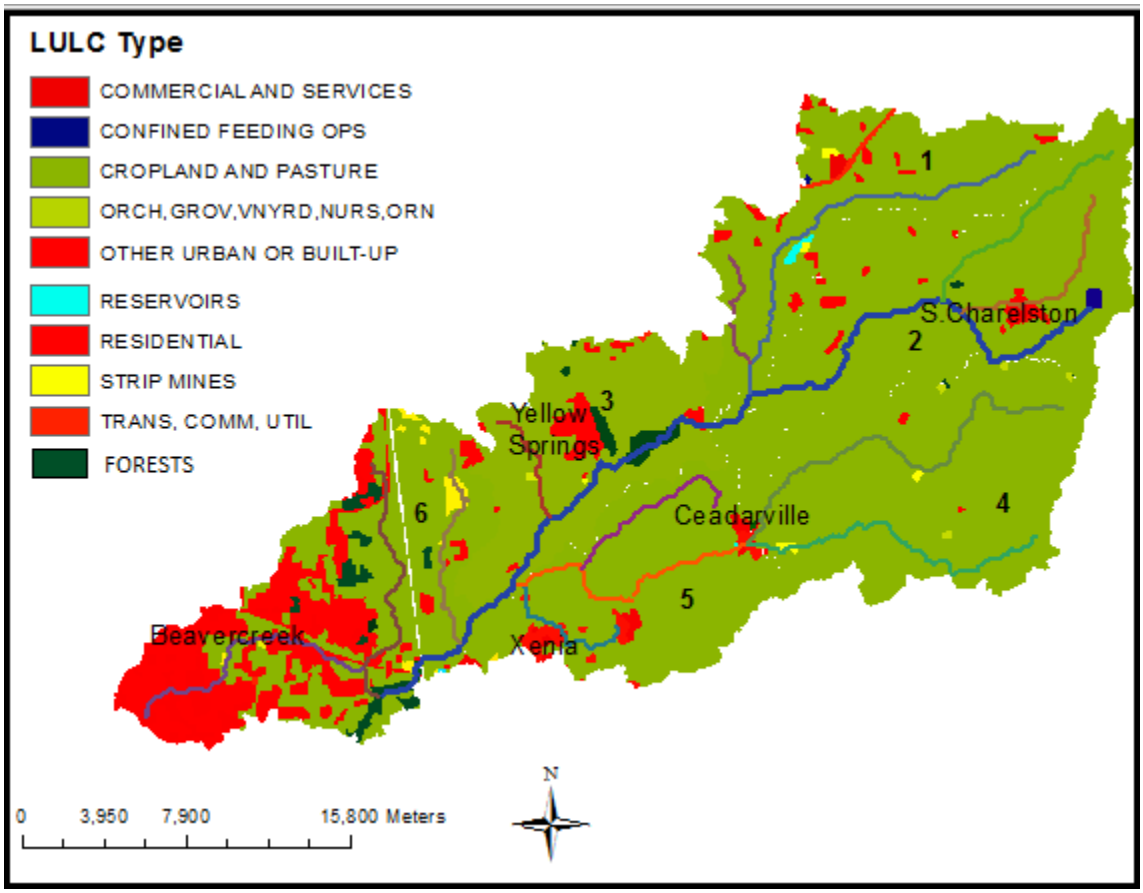


Figure 2.3 Land Use /Land Cover map for the study area of Upper LMR sub- Basin.

LULC	Percentage Area
Residential	9.88
Urban/Industrial	1.88
Cropland/Agriculture	85.48
Forest	1.82
Strip Mines	0.78
Confined Operations	0.11
Reservoir	0.04

Table 2.1 Percentage area of various LULC in the study area

LULC around the headwaters of the Little Miami River near South Charleston drains the catchment 2 and the north fork little Miami drains the catchment 1 of this study area. Both of these areas are predominantly agricultural. The waters here are affected by nutrient enrichment from agricultural runoff, changes in the habitat, uncontrolled livestock runoff, sedimentation and effluents from WWTP of South Charleston.

Catchment 3 consists of significant urban and forest land use. The North Fork Massie Creek which drains the catchments 4 and 5 of the study area and it is affected by sedimentation due to channelization and the absence of riparian buffers and hence acts as a nutrient-rich sediment source emanating from the vast areas of agricultural lands into to the Cedarville Reservoir. Beavercreek and Little Beavercreek drains the catchment 6 and majorly influenced by urban runoff and WWTPs. This section talks about various water quality indicators and its distribution patterns across various catchments.

2.4.1 Catchments- 1, 2

Little Miami River receives head waters from around the South Charleston area and the land use here is dominated by agriculture. The streams that are part of the head waters are the North Fork Little Miami and Lisbon Fork (Figure 2.4). These catchments are characterized by the lack of Riparian buffers and the river receives runoff from agricultural fields, discharge from South Charleston waste water treatment plant and also from the unfenced livestock runoff (Ohio EPA, 2002). The maps for catchment 1 and 2 are shown in Figure 2.4. Large scale cattle feeding operations are found in this region with the scope of further expansion. Based on the previous reports there have been contaminated discharges running into the streams (Ohio EPA, 2002).

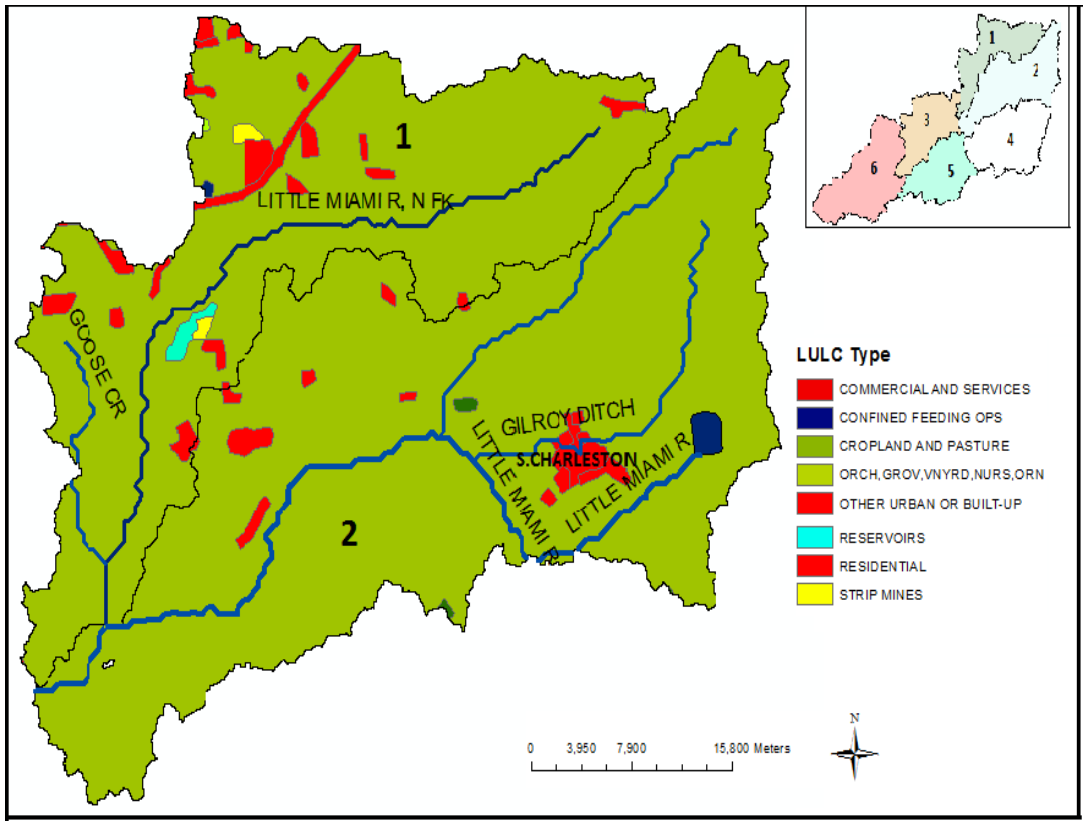


Figure 2.4 LULC map of Catchments 1 and 2.

2.4.2 Catchment- 3

This portion of the river in the catchment 3 receives waters from the Glen Helen Preserve of the Yellow Springs locality and runs through Little Miami Preserve and John Bryan State park. About 4 % of the total area is forested and about 8 % is urbanized and the rest is agriculture. Ludlow creek drains portion of this catchment, which mostly runs through agricultural land scape. The LULC distribution can be seen on Figure 2.5 below.

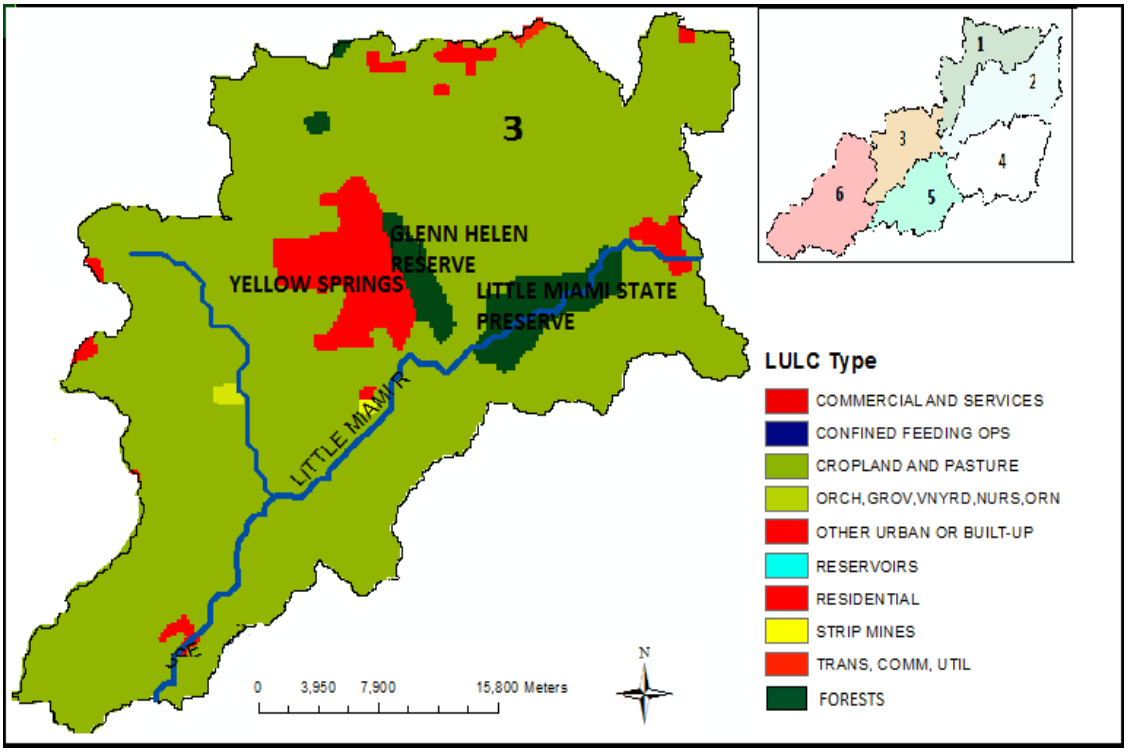


Figure 2.5 LULC map of Catchment 3.

2.4.3 Catchment- 4 and 5

Massies creek including north and south fork drains catchment 4 and 5 (Figure 2.6). Catchment 4 consists of more than 95% of agricultural landscape and also the town of Cedarville is located in this catchment area. This region is devoid of riparian buffers hence causing sedimentation in the streams and also resulting in algae growth in the

Cedarville reservoir due to agricultural runoff. The Cedarville waste water treatment plant discharges its treated water into the Massie creek after both the north and south fork merges at about the town of Cedarville.

Shawnee creek runs across the town of Xenia and the water quality of this stream is influenced by the urban land scape. This portion between and also receives effluent discharge from the Xenia waste water treatment plant. The town of Wilberforce is also located in this catchment area. About 7 % of the total area is urban area that includes the Cities of Xenia and Wilberforce.

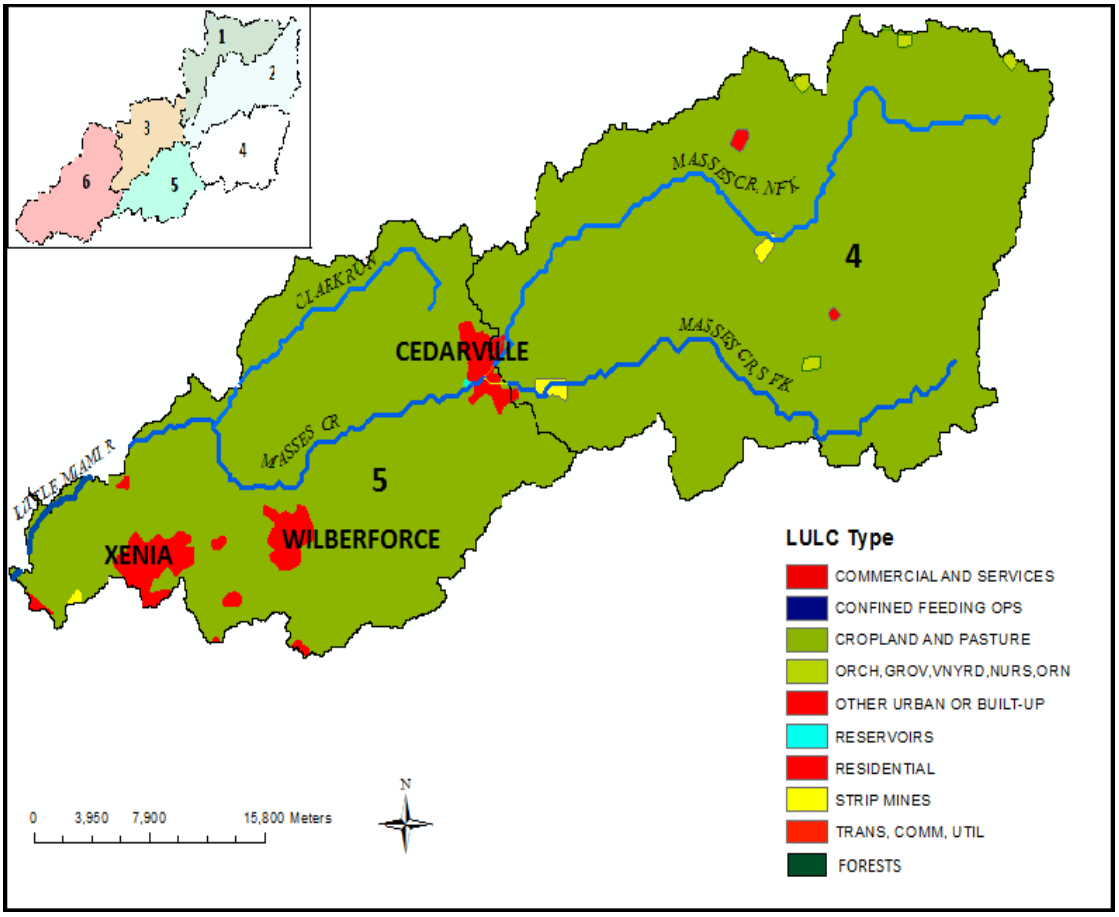


Figure 2.6 LULC Map of Catchment 4 and 5.

2.4.4 Catchment- 6

This region is important for this study as the Beavercreek and Little Beavercreek run mostly across urban landscape. This catchment has about 35 % urban areas and has a major influence on the quality of water. The Beavercreek area (Figure 2.7) is the largest city in Greene county, Ohio and second largest suburban area of Dayton. In 2007 it was ranked 84th in Money magazine's top 100 places to live, and hence this city is one of the most sought after location for living ("Beavercreek", Wikipedia, 2007). Understandably, the percentage of urban areas will tend to increase while agricultural activity around this area shall shrink due to urbanization. The little Beaver Creek receives discharge from Montgomery County Eastern Regional waste water treatment plant, which is supposedly the largest treatment plant in the upper little Miami Basin. Thus the streams carry much nutrient from the urban runoffs (Ohio EPA, 2002).

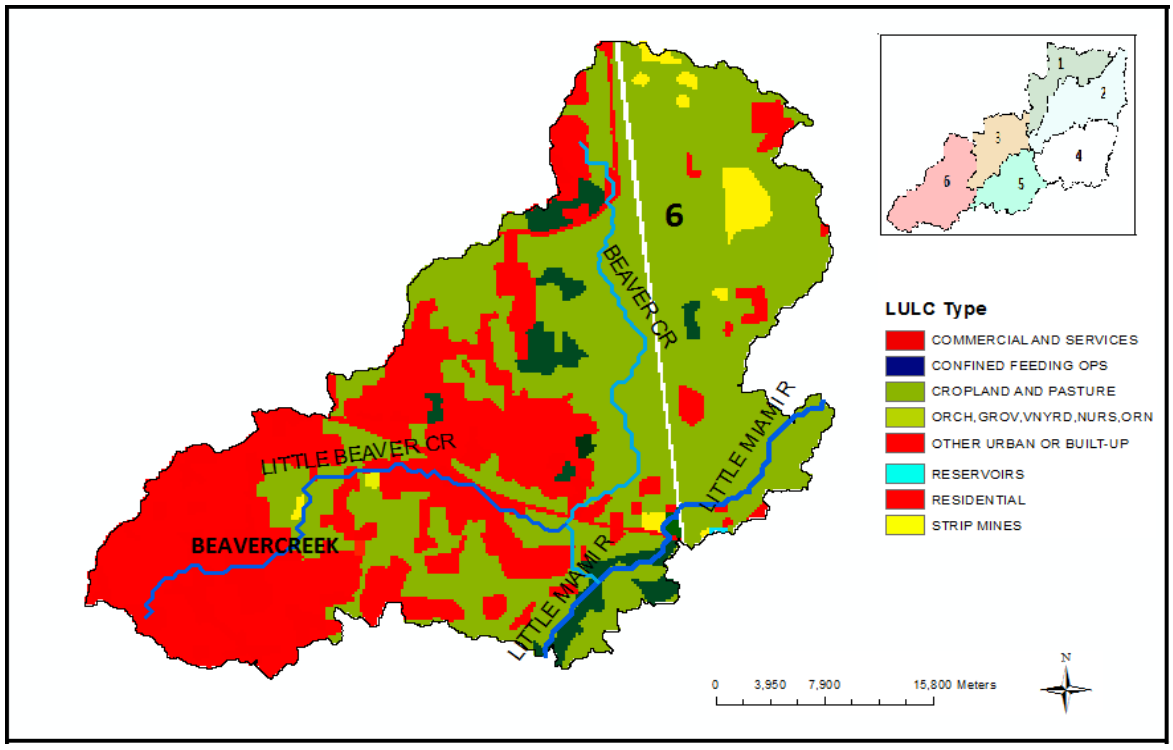


Figure 2.7 LULC Map of catchment 6.

2.5 Soil maps of the study area

Many soil properties, such as drainage, runoff, organic matter etc., could influence the water quality through leaching of solutes, detachment of soil particles, and chemical interactions between soil and water. Figure 2.8 shows the soil map with organic matter distribution of the study area. The process to generate this map will be discussed in section 3.6.

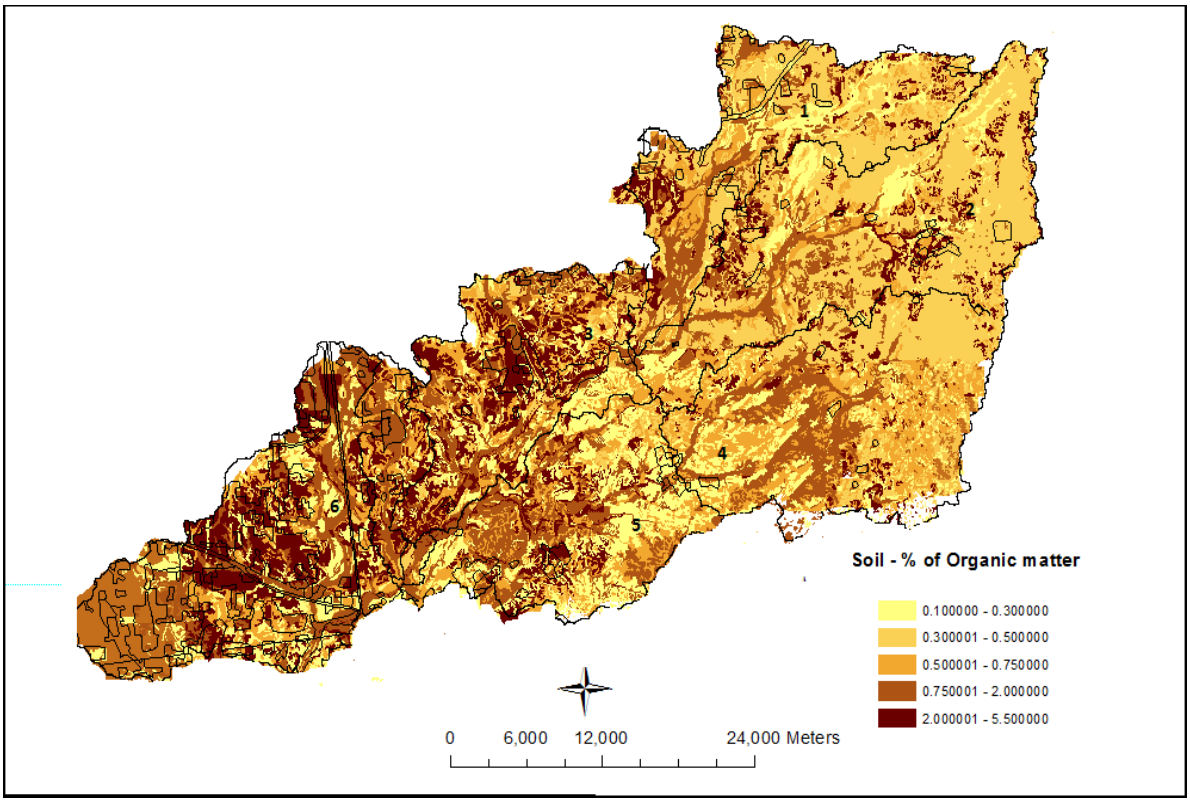


Figure 2.8 Soil map of the study area.

3.0 METHODOLOGY

3.1 Preparation and Field Methods

Six sampling outlets for 6 different major catchments were selected based on watershed delineation using BASINS 4.0 Twenty-six other sampling locations were identified across smaller streams that drain the entire study area. Using Google maps and other coordinate applications on a smartphone the locations were identified on the field. YSI 6600 V2 multi-probe sonde was used for measuring water quality parameters in the field. This instrument measures pH, temperature, dissolved oxygen, specific conductance, redox potential and turbidity. This instrument was calibrated with the solutions provided by the manufacturer before every sampling event in order to get accurate results.

Bottles used for sampling were washed with 2% HCL acid solution and rinsed with deionized distilled water. The bottles were numbered in chronological order and the water samples were collected from selected outlet points designed from delineation. Two bottles of about 60 ml samples were collected by grab sampling. Before samples were collected the bottles were rinsed for at least 2 times with river water before doing the grab sampling. Collected bottles were placed in a cooler while being transported to the laboratory and then stored in the refrigerator until analysis. Samples were collected for

analysis of nitrate, phosphate (both total and orthophosphate), major ions, alkalinity, and silica using several methods such as spectrophotometer and ion chromatography.

3.2 Lab Work

3.2.1 Spectrophotometric method

The HACH chemical analysis kit was used for the analysis of Total Phosphate, nitrate and silica. This method is relatively easier and more accurate way of measuring the concentrations. Required proportions of water samples were mixed with provided reagents as per the procedure, the color that is generated from the sample-reagent mixture was measured at a particular wavelength for each chemical and the concentrations are expressed in mg/L. The accuracy of the instrument was assessed by preparing standard laboratory solutions of known concentrations and was measured using respective procedures of each chemical and by plotting the measured results against the standard concentrations and therefore obtains a curve of best fit for calibration.

3.2.1.1 Orthophosphate and Total Phosphate (TP)

Total Phosphates of the water samples were measured using HACH's PhosVer^{TM} 3 kit using acid hydrolysis principle. Phosphates present in various forms such as meta-, pyro-, or other polyphosphates were converted to reactive orthophosphate before analysis by pretreating the sample with acid and heat which hydrolyzes the condensed inorganic forms to orthophosphate. Orthophosphate is then allowed to react with molybdate in acidic conditions to form a molybdate complex. Subsequent reduction by the ascorbic

acid forms a blue color measured at 880 nm using a spectrophotometer expressed as PO_4^{3-} (HACH 8180).

3.2.1.2 Nitrate

NitraVer 5 nitrate reagent powder pillows from HACH were used for the measurements using the cadmium reduction principle. The entire nitrate is reduced to nitrite under acidic conditions nitrites forms diazonium salt. These salts react with gentisisic acid to produce amber/pale yellow colored which is measured at 500 nm using the spectrophotometer (HACH 8039). Results were calibrated with standard calibration curve for instrument accuracy. The values are reported as NO_3^-.

3.2.1.3 Silica

Silica was measured using HACH's silicomolybdate powder pillows method. Silica reacts with molybdate under acidic conditions to form silicomolybdate complexes which is pale yellow in color and are measured using spectrophotometer at 452 nm (HACH 8185).

3.2.1.4 Alkalinity

Alkalinity was measured using newer method designed by Sarazin et al. 1999. This method is extremely fast when compared to the gran plot method described by Drever (1997). This method works on principle of neutralizing all the basic species with weak acid (formic acid). A pH sensitive dye (bromophenol blue) in the mixture gives a color with intensity proportional to alkalinity measurable at 590nm using a

spectrophotometer (Sarazin et al., 1999). A standard calibration curve is used to establish the relationship between alkalinity and absorbance.

3.2.2 Ion chromatography method

Cations (calcium, magnesium, potassium, sodium) and anions (sulfate, chloride, fluoride) were all measured using an Ion Chromatograph(IC). Dionex ICS 2000 ion chromatograph equipped with IonPac® CS12 analytical and guard columns and SRS 300 electrolytic suppressor was used to measure amounts of the cations in the samples, whereas Dionex ICS 1500 equipped with IonPac® AS22 analytical and guard columns and SRS 300 electrolytic suppressor was used for anion analysis. The samples used in the analysis were filtered with the .22µm filter since the particles of size greater than .2µm hinders or rather clogs the chromatographic column machine. The samples along with the combined standards of various concentrations were run together and the results of the standards were used as the calibration curves for determining the concentrations of ions in the sample.

3.3 Hydrologic Modeling (BASINS)

Better Assessment Science Integrating point and Non-point Sources (BASINS) is a flexible hydrologic modeling tool that integrates GIS, watershed data, Hydrologic and Water quality stream models. The latest version of BASINS 4.0 uses the GIS shape files which can be shared with other GIS software. This latest version provides enhanced watershed analysis process by creating plugins.

The initial step using BASINS 4.0 is to download the data pertaining to the watershed. For this study the data for Little Miami river basin (HUC 05090202) was

downloaded. Then using watershed delineation tool catchments were defined within the basin. Six catchments were designed. The shapes and attributes were edited and the outlets for each delineated catchment were defined. The outlets were defined in such a way that they are located in the point where the water of that catchment is drained to that point as shown in Figure 3.1. The watershed boundaries were delineated based on the reach file (EPA, 2007), National Hydrography Dataset (NHD) flow lines (USGS, 2009), and the catchment file.

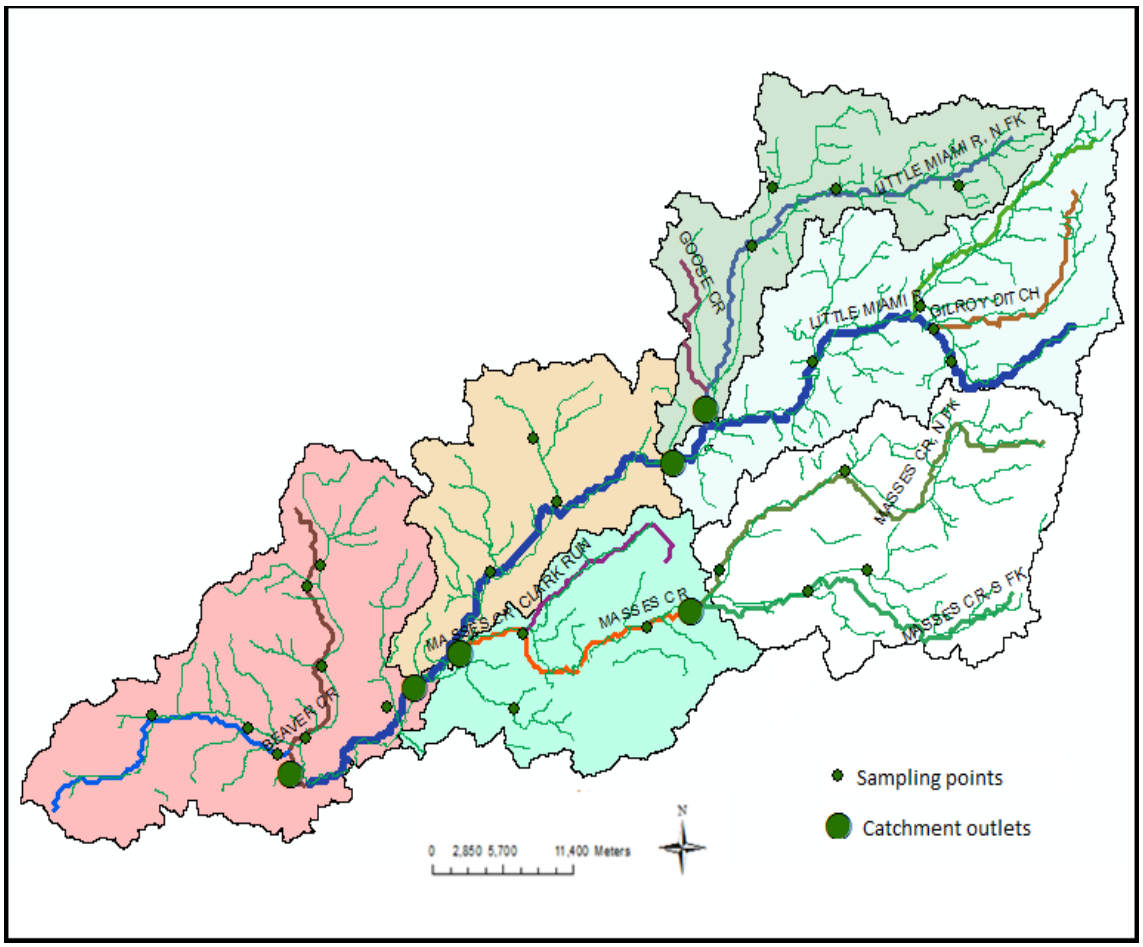


Figure 3.1 Catchment outlets and sampling locations.

3.4 Spatial Analyst tool (ArcGIS)

Zonal statistics tool of Spatial Analyst extension for ArcGIS 10.0 software was used to process LULC and soil data within each sub-watershed in the Little Miami River sub- Basin. The land cover was classified into 4 broad groups. Urban category includes residential and commercial land uses. Agriculture category includes crops, vineyards and orchards. The third category is forest and all others are grouped as "others". The "others" group has small percentage of various land use types such as reservoirs, confined feeding operations, and strip mines, which are essentially gravel pits. Histogram option of zonal statistics was used to calculate the percentage area of all the land use types within each catchment in terms of acreage. Table 3.1 summarizes the LULC distribution in each catchment.

Group	**LULC type**	**Catchments**					
		1	2	3	4	5	6
Urban	Residential	3.36	1.29	5.42	0.33	3.90	31.61
	Urban/commercial	2.81	1.28	1.73	0.09	2.87	3.20
Agriculture	Cropland	92.51	96.72	87.62	98.68	93.06	59.08
	Vineyards/Orchards	0.06	-	0.26	-	-	-
Forest	Forests	-	0.19	3.71	0.41	-	4.30
Others	Confined feeding ops	0.11	0.52	-	-	-	-
	Reservoir	0.61	-	-	-	0.05	0.04
	Strip Mines	0.54	-	1.25	0.49	0.11	1.78

Table 3.1 Percentage area of LULC in the study area

3.5 Calculating production coefficient using linear matrix multiplication

$$c_i = \sum_{j=1}^{m} a_{ij} \cdot p_i \qquad \textbf{Eq. 1}$$

As per the assumption, the solute concentrations at the outlet of the catchment should be the product of mixture of leachates from each LULC within the catchment and its production coefficient as per shown in Equation 1. Regression modeling is used to calculate the concentrations (c_i) of nutrient/solute load at a given outlet of the each catchment that is influenced by the land use in that particular catchment. These coefficients are expressed in terms of mg/l/per acreage percent and are termed production coefficients. These coefficients were calculated using linear matrix multiplication modeling explained as follows.

$$P_{M*1} = \begin{pmatrix} P_1 \\ P_2 \\ . \\ P_M \end{pmatrix} \qquad C_{N*1} = \begin{pmatrix} c1 \\ c2 \\ . \\ cN \end{pmatrix}$$

Where, $P_{i's}$ are nutrient production coefficients for each land type i.e. production of nutrient per percent fraction of land. M is the total number of land use types. $C_{i's}$ are concentrations of nutrients at N different sub-watersheds.

$$A_{N*M} = \begin{pmatrix} a_{11}\ a_{12}\ \ldots.\ a_{1M} \\ a_{21}\ a_{22}\ \ldots.\ a_{2M} \\ a_{31}\ a_{32}\ \ldots.\ a_{3M} \\ a_{N1}\ a_{N2}\ \ldots.\ a_{NM} \end{pmatrix}$$

Where, a_{ij} gives the acreage percentage of i land type in j watershed.

Each row of the matrix A_{N*M} determines the acreage percentage of each of the M different land use types within a catchment. The solute concentration matrix is a product of matrix A and matrix B.

$$\mathbf{C_{N*1} = A_{N*M}. P_{M*1}} \qquad \textbf{Eq.}\ 2$$

Values of the C_{N*1} matrix will be determined from the amounts of nutrient/solute measured at catchment outlets.

Since the study has 6 catchments and therefore represents 6 linear equations written in matrix form. For this study the following matrix multiplication formulae was used to calculate the production coefficients for each land use types of matrix B.

$$\mathbf{A_{6*4}\ .\ P_{4*1} = C_{6*1}} \qquad \textbf{Eq.}\ 3$$

Where,

Matrix P_{4*1} - Coefficients of 4 groups of LULC (Urban, Residential, Forest, and Others)

Matrix C_{6*1}- Conc. of solute at the outlet of each of the 6 catchments

Matrix A_{6*4}- Acres of land of the 4 groups of LULC in 6 catchments

Equation 2 now can be re-written as:

$$\mathbf{P = (A)^{-1}. C} \qquad \textbf{Eq.}\ 4$$

The above matrix multiplication formula represents an over determined system with 4 unknowns in 6 linear equations and there would be no unique solution for this problem. The least square regression method is therefore needed. Regression using least squares gives the best fit for all the curves plotted using linear equations. Based on the linear regression for matrix multiplication formula, the equation 4 is now expressed as follows,

$$\mathbf{P = (A^tA)^{-1}. A^t.C} \qquad \textbf{Eq.}\ 5$$

The solution for Equation 5 is a 4*1 matrix**.** Using this formula, regression analysis can be done for the estimation of nutrient concentrations starting from smaller sub basins to larger sub basins and to the river basin as a whole.

3.6 Soil Maps

Other than LULC, soil types could also influence surface water quality. Soil maps were generated from SSURGO data downloaded from the NRCS website (http://soildatamart.nrcs.usda.gov/Survey.aspx). These maps were used to analyze how the soils in the region influence water quality. Soil properties such as runoff, slope, soil horizons and organic matter are potentially the major soil parameters that could affect water quality.

The website allows the user to select the area based on the counties and sends a download link to the user via email. Using the link the spatial data as well as tabular data which are required for generating soil maps were downloaded. The customization of the required tabular data was done by using the Microsoft Access database which lets the user to create queries and allows the user to generate the specific tabular data in the Excel file format. Once the Excel file was generated and it was saved as .dbf extension, later this file was added on to the ArcGIS tool as a layer and is joined with respective spatial data to form the soil map layer.

The soil maps for the distribution of silt, clay, the extent of runoff, extent of drainage type were customized using the access query and a excel sheet in the form of .dbf file were generated. Once the spatial data for the county is added on to the ArcGIS the tabular data is joined with the spatial data to generate maps. Appendix F, lists the detailed steps.

3.7 Pearson's Correlation Matrix for water quality variables

Pearson's matrix was created for the water quality variables to determine the relationships amongst the variables in the catchments and the water quality of the streams. The R^2 value gives the magnitude and direction of correlation amongst those variables. These R^2 values can range from -1 to 1. Values from -0.5 to -0.01 and values from .01 to 0.5 generally mean weak or no relationship whereas values from – 1 to -0.5 and 0.5 to 1 indicate strong negative and positive correlations, respectively. These correlations can be due to a cause-effect relationship, a common geochemical reaction, or it might just be a mere coincidence and might not have any significance with that number.

3.8 Stability Diagrams

These diagrams were constructed in order to understand the mineral equilibria in the natural waters of the Upper Little Miami River. Measured concentrations of solutes such as silica and other ions from the water samples were used in obtaining solute activities using PHREEQC software (USGS, 2011). This software is USGS proprietary program for geochemistry calculations. The activities of the silica and other ions were plotted on the stability diagrams to study the impact of mineralogy on water chemistry. Two different mineral systems, K_2O- SiO_2-H_2O-Al_2O_3 and CaO-SiO_2-H_2O-Al_2O_3, were used in the study.

4.0 RESULTS AND DISCUSSION

This section represents the results of water quality study to evaluate relationships between nitrate and total phosphate concentrations, silica, ions and watershed characteristics in the Upper LMRB. Results are divided into various sections 1) GIS analysis using Zonal statistics, 2) Water quality at each catchment area and land use influence, 3) production coefficient of various for various solutes in the water, 4) water chemistry correlations, and 5) Influence of soil on water quality using soil maps, and 6) silica stability relationship

4.1 GIS Analysis Using Zonal Statistics

Using the data downloaded with BASINS 4.0, the datasets, such as hydrology and LULC, were used to delineate the catchments using Digital Elevation Models (DEM) and drainage boundaries. The LULC was classified into 4 broad groups as urban, agricultural, forests and others. Others group is the summation of many smaller constituents of the catchment including confined feeding operations, reservoirs and strip mines. Using the GIRAS land use database and the zonal statistics tool of ArcGIS, the constituent percentage of each of the catchments were calculated. Figure 4.1 and table 4.1 summarize the results.

As mentioned earlier, the predominant land type of the study area is agriculture. Catchment 6 is the only one with very high urban area; it contains about 35% of the total area as shown in table 4.1. Forest lands are significant in catchments 3 and 6.

Catchment 6 is divided into 6a and 6b to further segregate the LULC distribution for a better range of urban %.

Catchment	Urban area	Agriculture area	Forest area	Others
1	6.17	92.57	0.00	1.16
2	2.57	96.72	0.19	0.52
3	7.15	87.89	3.71	1.25
4	0.42	98.68	0.41	0.49
5	6.77	93.06	0.00	0.17
6	34.82	59.09	4.30	0.82
6a	83.25	13.37	3.38	0.00
6b	8.36	82.44	5.85	3.35

Table 4.1 Percentage distribution of LULC In each catchment area

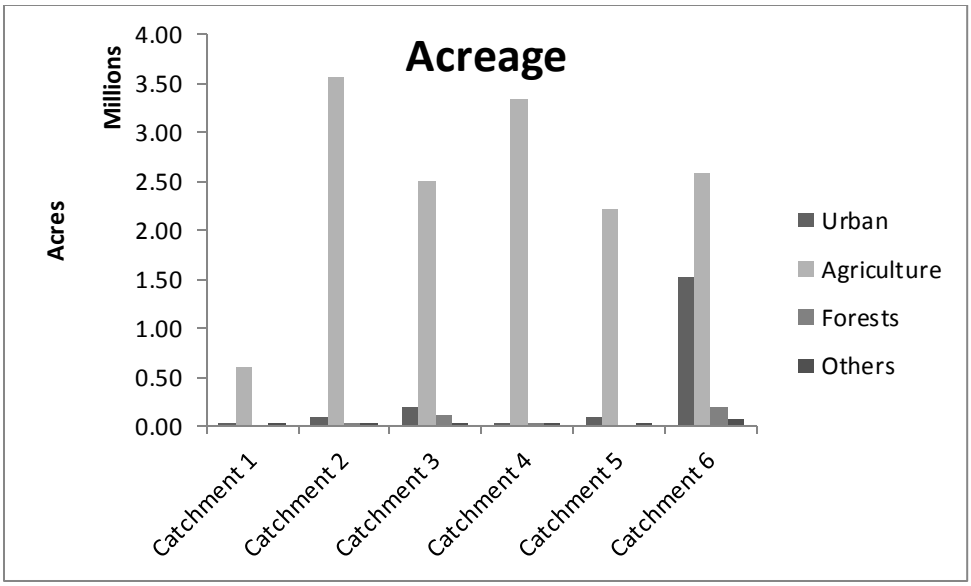


Figure 4.1 Acreage distribution of LULC within catchments.

4.2 Water quality

Nutrients and water chemistry from each of the 32 sampling locations are presented in this section. Table 8.2.1 and Table 8.2.2 in Appendix A list the analytical results for water samples and Table 4.2 summarizes nutrient, field data and alkalinity by each catchment.

Catchment	Value	Nitrate (mg/L)	TP as PO_4^- (mg/L)	Silica as SiO_2 (mg/L)	pH	Conductivity (µS/cm)	Turbidity (NTU)	DO (mg/L)	Alkalinity (mM/L)
1	min	1.9	0.19	7.6	8.10	618	2.2	11.24	5.73
	max	3.4	0.41	20.4	8.27	681	12.5	14.01	6.94
	mean	3.0	0.26	11.6	8.12	655	5.3	12.62	6.53
	median	2.5	0.25	9.2	8.25	657	4.1	12.76	6.76
2	min	3.2	0.20	8.4	8.09	659	1.7	10.4	5.94
	max	3.9	0.37	20.3	8.38	795	14.9	11.77	6.88
	mean	3.5	0.29	13.5	8.24	699	5.6	11.10	6.41
	median	3.4	0.29	12.6	8.23	671	2.9	11.11	6.40
3	min	2.0	0.31	11.1	7.95	626	3.7	9.93	6.18
	max	4.4	1.19	28	8.31	655	165	14.11	6.94
	mean	2.8	0.57	17.2	8.08	644	39.8	11.43	6.55
	median	2.4	0.38	13.3	8.05	648	6.8	10.42	6.51
4	min	2.7	0.16	4.5	7.92	592	1.8	12.09	6.92
	max	3.5	0.21	8.6	8.03	651	3.5	16.57	6.96
	mean	3.1	0.18	6.6	8.13	631	2.5	14.44	6.95
	median	3.1	0.18	6.7	8.14	641	2.3	14.55	6.95
5	min	2.8	0.19	5.4	8.00	380	2.6	9.90	5.40
	max	3.6	0.60	10.1	8.23	677	53.1	12.07	6.96
	mean	3.1	0.32	7.8	8.18	615	20.3	10.79	6.44
	median	3.0	0.24	7.8	8.23	590	5.4	12.07	6.94
6	min	0.7	0.13	3.2	7.44	560	1.6	9.02	4.36
	max	3.2	1.05	13.6	8.24	817	275	12.08	6.96
	mean	2.0	0.55	9.7	7.98	728	43.5	10.19	6.14
	median	1.5	0.39	11.2	7.98	762	12.6	10.08	6.39

Table 4.2 Summary of nutrients, field data and alkalinity by each catchment

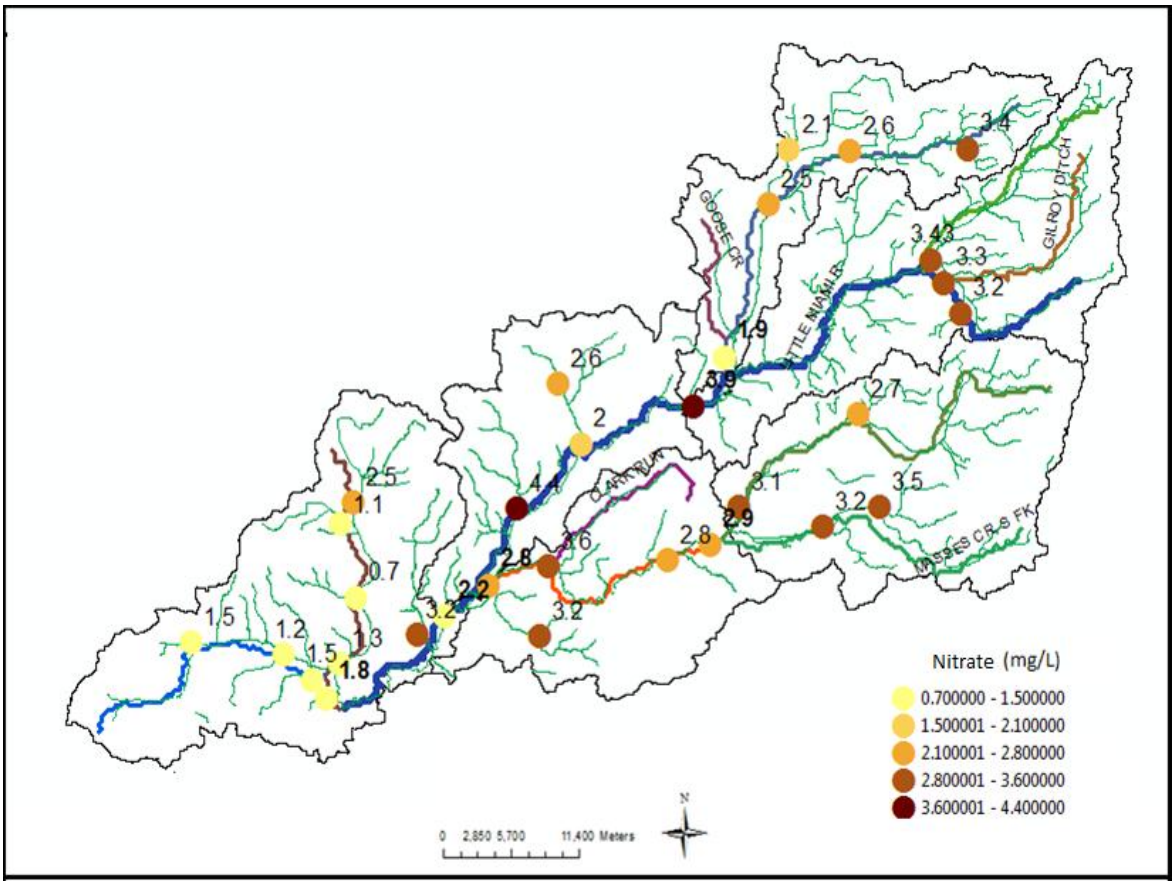


Figure 4.2 Spatial distribution of nitrate at various locations of the study area.

Figure 4.2 shows the spatial distribution of nitrate across the study area at various locations of each catchment and its outlets. As a result of nutrient loading due to runoff from agriculture the mean levels of nitrate are seen to be in elevated levels in the catchments 1-5.

Mean nitrate concentrations range from 2.8 – 3.46 mg/L across the catchments 1-5, Agriculture land is most likely the major source. Catchment 6 has a mean concentrations of about 2.03 mg/L which is much below the average concentrations of other catchments. The streams in catchment 2 and 4 are influenced by lack of riparian buffers(Ohio EPA, 2002), which could otherwise prevent the agricultural runoff running into the streams directly.

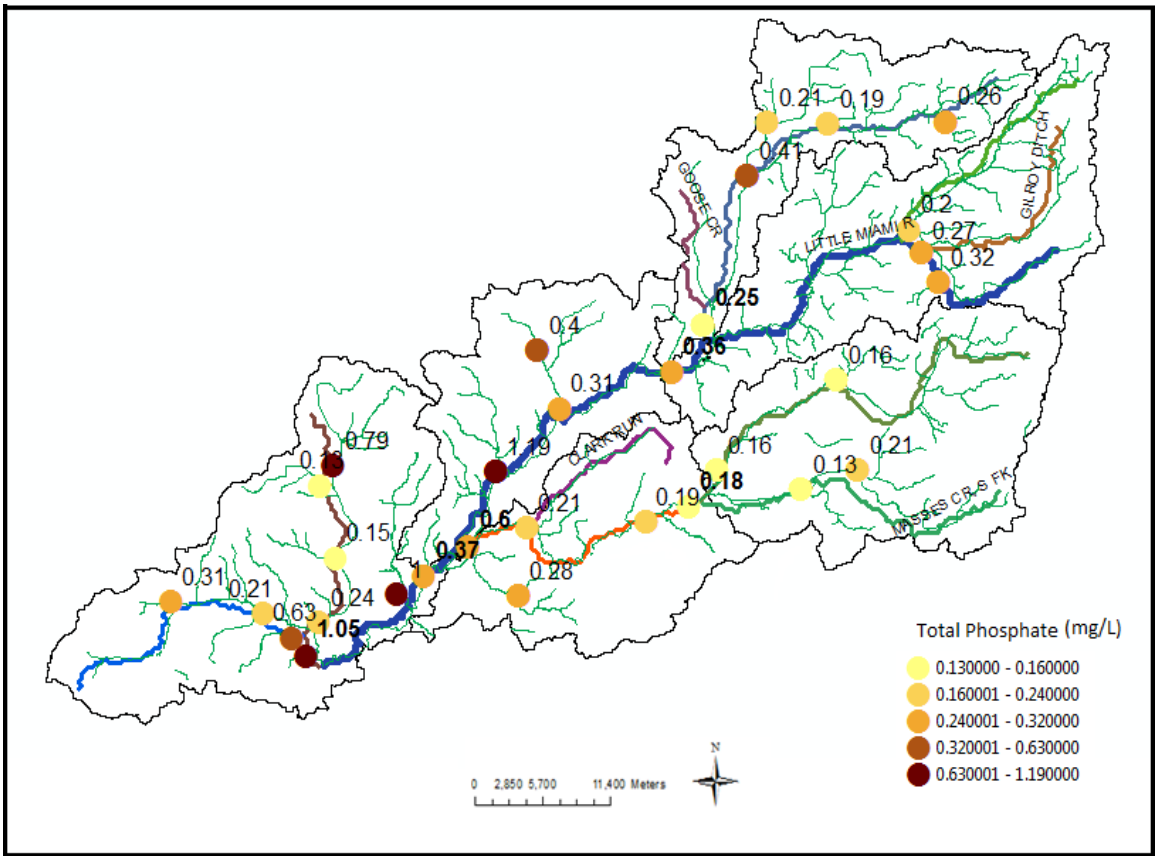


Figure 4.3 Spatial distribution of Total phosphate(TP) at various locations of the study area.

Figure 4.3 shows the spatial distribution of Total Phosphate (TP) across the study area. Catchments 3 and 6 have greater mean values of TP levels at about 0.56 mg/L than that of other catchments. The Little Beaver Creek in the catchment 6 is influenced by urban runoff and channelization. The discharge by the Montgomery County Eastern Regional WWTP discharge in the downstream may also affect stream water quality. This catchment is predominantly urban with about 35% percentage of the total catchment area. Interestingly the streams draining the catchment area 6 are rich in TP concentrations and the mean level is at 0.56 mg/L, but nitrate concentrations are relatively low at mean levels of 2.03 mg/L (Figure 4.4).

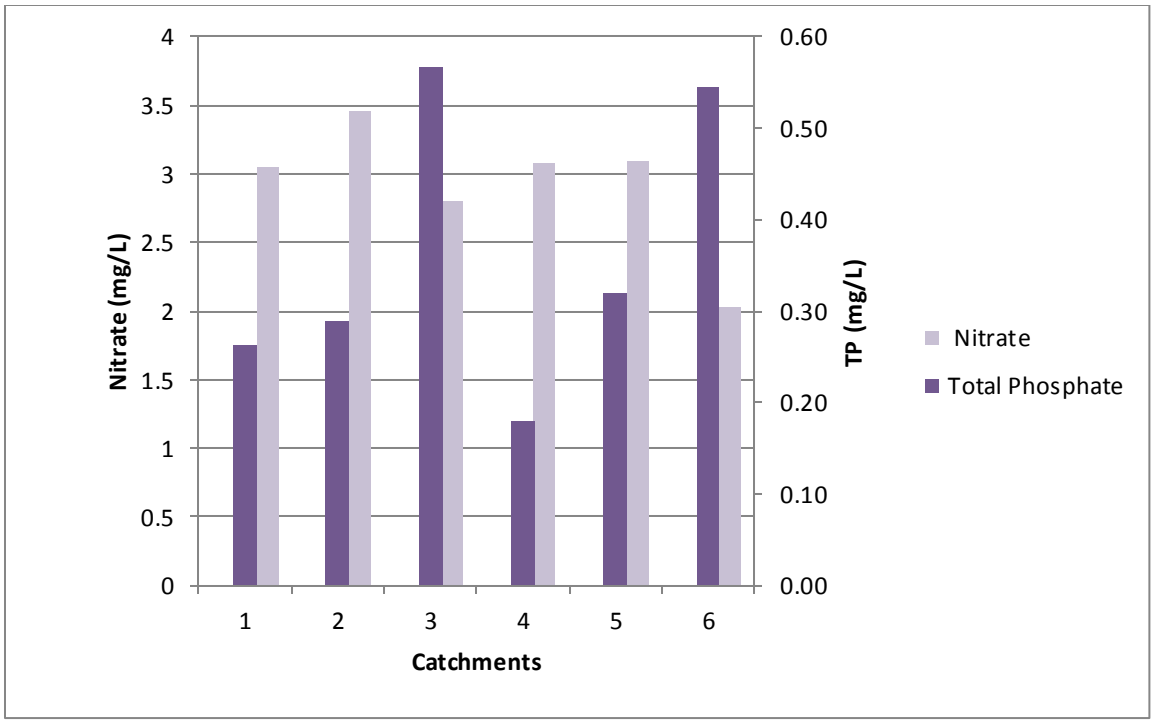


Figure 4.4 Mean concentrations of nutrient in each catchment.

The catchments with higher percentage of urban areas (in brackets) are catchment 5 (6.77%), catchment 3 (7.15%) and catchment 6 (34.82%). These catchments had greater mean TP concentrations in their streams. As a result, there were greater amounts suspended particles in water. Hence, increasing the mean turbidity levels of these streams as shown in Table 4.2. The mean dissolved oxygen levels at 21° C of about 12.7 mg/L of the sampling points on the North fork little Miami of catchment 1 is a clear indication of super saturation of oxygen due to photosynthesis by algae, whose growth is influenced by nutrient upload in the streams.

4.2.1 Correlation among the water quality parameters

Median values for water quality indicators were used in the analysis for this correlation study instead of mean values. This is to reduce the effects of a certain extreme high or low values of certain samples which might show a wrong correlation

Pearson's correlation matrix (Table 4.3) shows the correlation among water quality indicators and the percentage area of urban and agriculture areas. This matrix also includes the percentages of urban and agriculture land use to see whether various parameters can be directly linked to the land use type. The labels (1-6) on the chart indicate the catchment number.

	Nitrate	Total P	pH	Sp. Cond.	TU	DO	Temp.	Chl.
% Urban Area	**-0.81**	**0.47**	**-0.67**	**0.67**	0.16	-0.39	0	0
% Agriculture area	**0.87**	**-0.55**	0.04	**-0.58**	-0.24	0.37	-0.04	0

Table 4.3 Pearson's Correlation matrix for watershed variables and % of agriculture and % urban land-use, the values are shown as r^2 values showing the strength and direction of correlation. The values in bold represent statistically significant values but not necessarily have a cause-effect relationship.

The parameter pairs that have significant correlations are shown in bold. High correlation values may indicate a significant cause-effect relationship or a common factor.

Figure 4.5 shows correlation between TP and % urban area and Figure 4.6 shows correlation between nitrate and urban areas. Even though we have seen the trend of higher levels of TP in the urban streams, the correlation matrix does not show greater

strength in relationship but definitely shows a positive correlation (R^2=0.47) signifying the likely impact of urban areas on total phosphate loading.

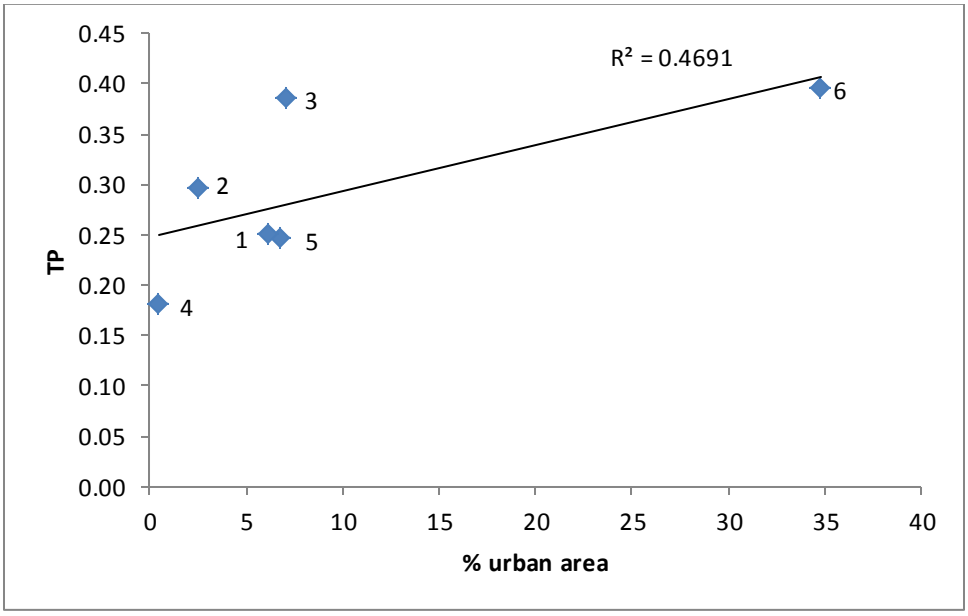


Figure 4.5 Correlation between median total phosphate concentrations and the % of urban area in the catchments.

However the positive trend seen between % urban areas and phosphate loading may also be due to the fact that the presence of WWTP in the catchments might give a false representation of results as the treatment plants tend to get discharges from various sources (Ahearn et al., 2005; Bolstad et al., 1997).Strong but negative correlation (R^2= -0.81) (Figure 4.6) between % urban and nitrate concentrations suggesting that more the urban areas lesser the nitrate production from the catchment. This trend is similar to the one seen in one of the earlier studies in the little Miami River basin (Tong and Chen, 2002).The negative correlation(Figure 4.6) is directly related to the lack of agriculture runoff(fertilizers) carrying nitrate.

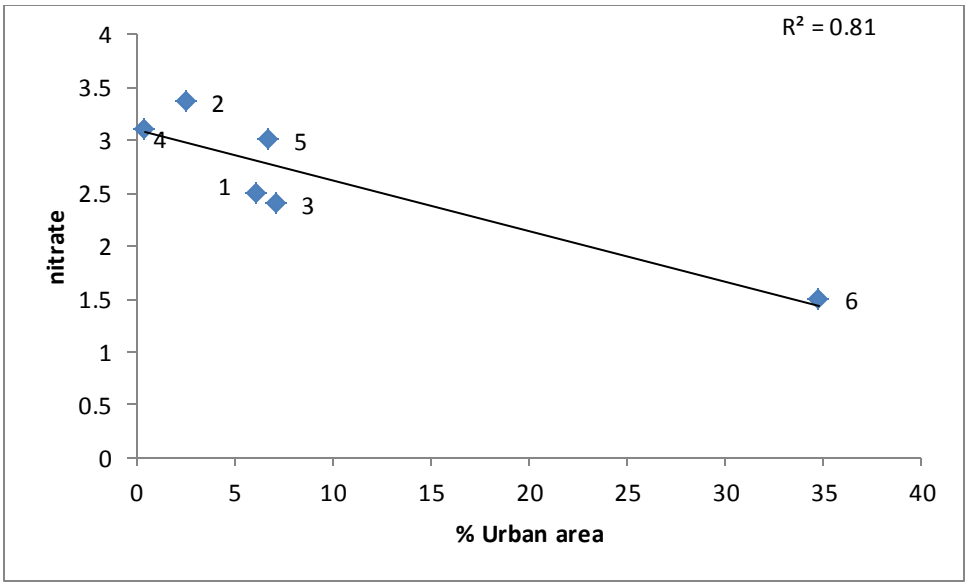


Figure 4.6 Correlation between median nitrate concentrations and the % of urban area in the catchments.

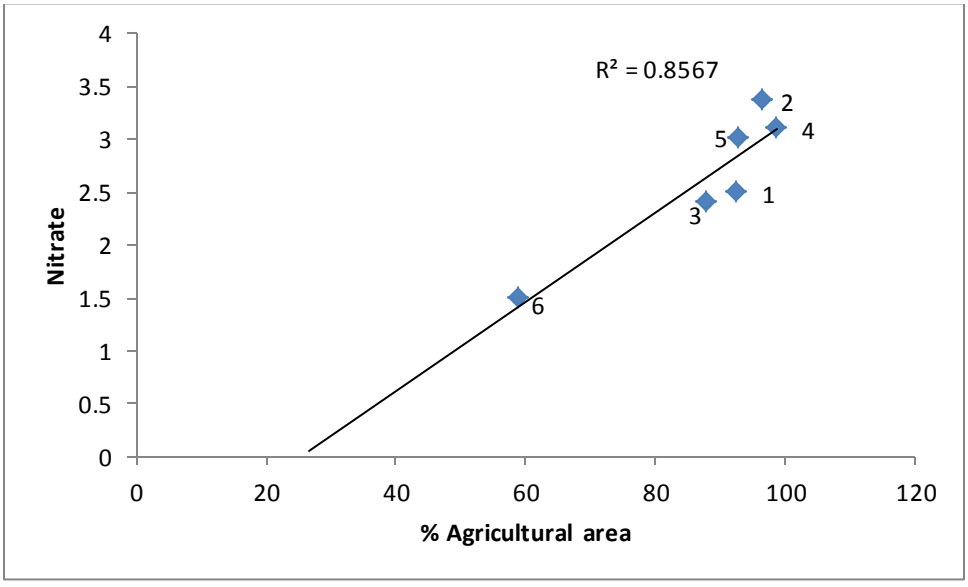


Figure 4.7 Correlation between median nitrate concentrations and the % of agriculture area in the catchments.

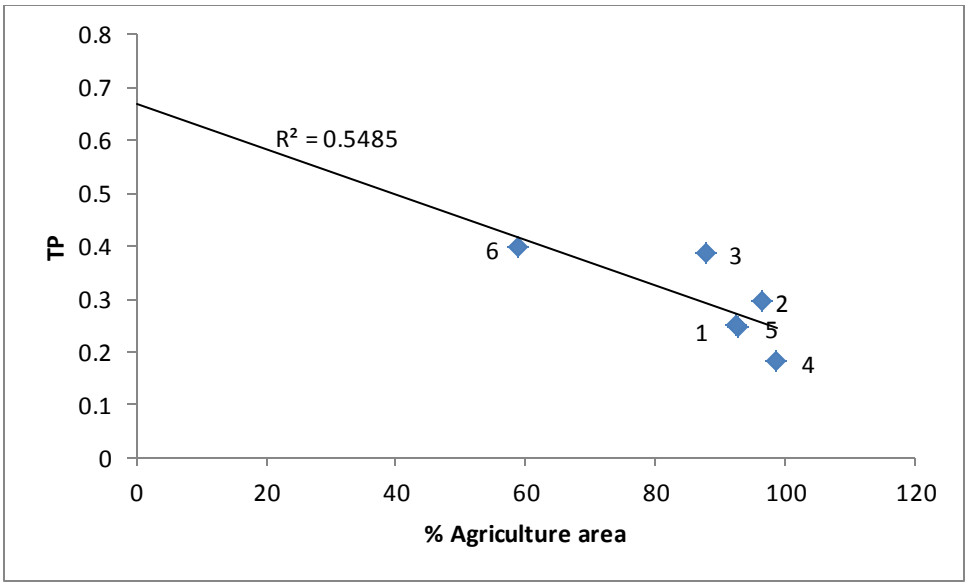


Figure 4.8 Correlation between median total phosphate concentrations and the % of agriculture area in the catchments.

Agriculture areas show greater positive correlation with nitrate production as seen in Figure 4.7. This trend may be due to the seasonal application of nitrate rich manure to the fields for crop production (Brett et al., 2005; Ahearn et al., 2005) or nitrate fertilizer.

Table 4.4 shows the pearsons correlation matrix for watershed variables. Strong correlation (R^2= 0.86) (Figure 4.7) between the % agriculture area and nitrate concentrations and a moderate positive correlation (R^2= 0.58) between the DO and nitrate (Figure 4.9) supports influence of photosynthesis. High % of agriculture produce high nitrate, high nitrate promotes photosynthesis. During photosynthesis, phosphate and CO_2 is consumed. The extent of photosynthesis may also affect the relationship between pH and % urban area. There is a moderate negative correlation (R^2=-0.52) between pH and the % urban areas (Figure 4.10). Similar relationship was also observed in a water quality study in Arkansas (Borchelt, 2007). However, negative correlation exists between TP and

% agricultural land in the catchment (Figure 4.8). This trend is due to consumption of TP during photosynthesis.

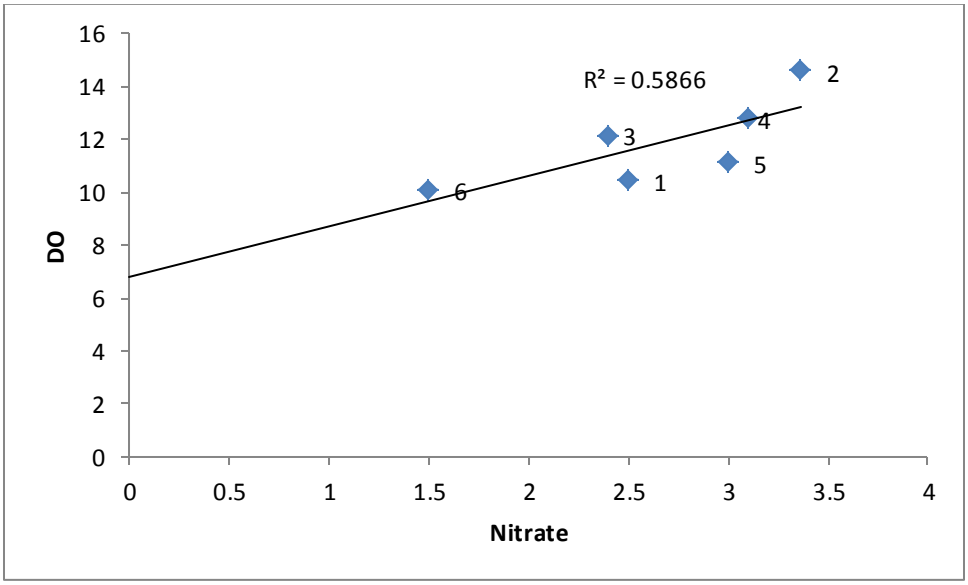


Figure 4.9 Correlation between median nitrate concentrations and DO concentrations in the catchments.

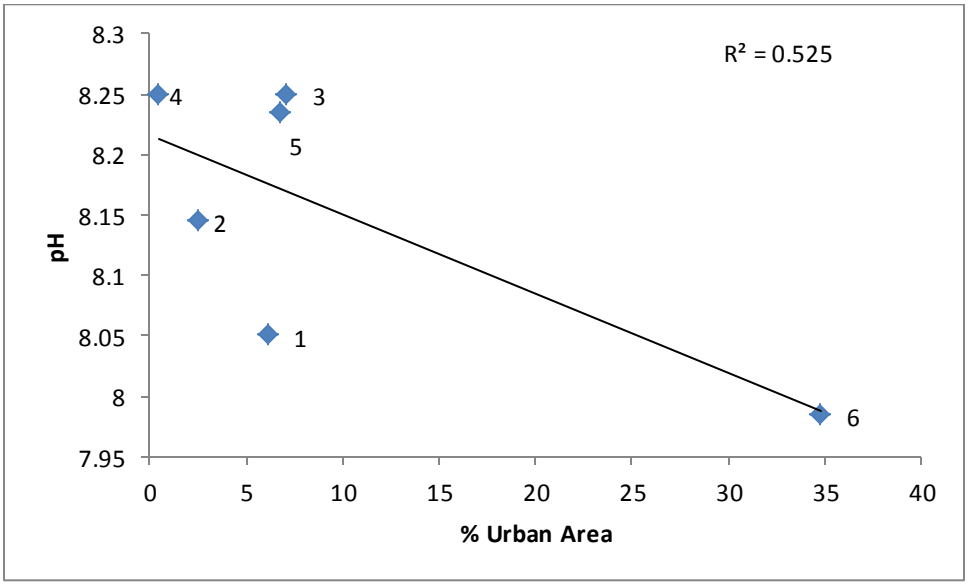


Figure 4.10 Correlation between median pH values and % urban area in the catchments.

	Nitrate	Total P	pH	Sp. Cond.	TU	DO	Temp.	Chl.
Nitrate	1							
Total Phosphate	**-0.50**	1						
pH	**0.46**	-0.15	1					
Sp. Conductivity	-0.33	0.03	**-0.47**	1				
Turbidity(TU)	-0.44	**0.61**	0	-0.03	1			
DO	**0.59**	-0.05	0.26	-0.26	**-0.50**	1		
Temperature	0	0.07	-0.03	0	0	0.42	1	
Chlorophyll	-0.12	-0.01	0.02	-0.03	0.20	-0.42	-0.43	1

Table 4.4 Pearson's Correlation matrix for watershed variables, the values are shown as r^2 values showing the strength and direction of correlation. The values in bold represent statistically significant values but not necessarily have a cause-effect relationship.

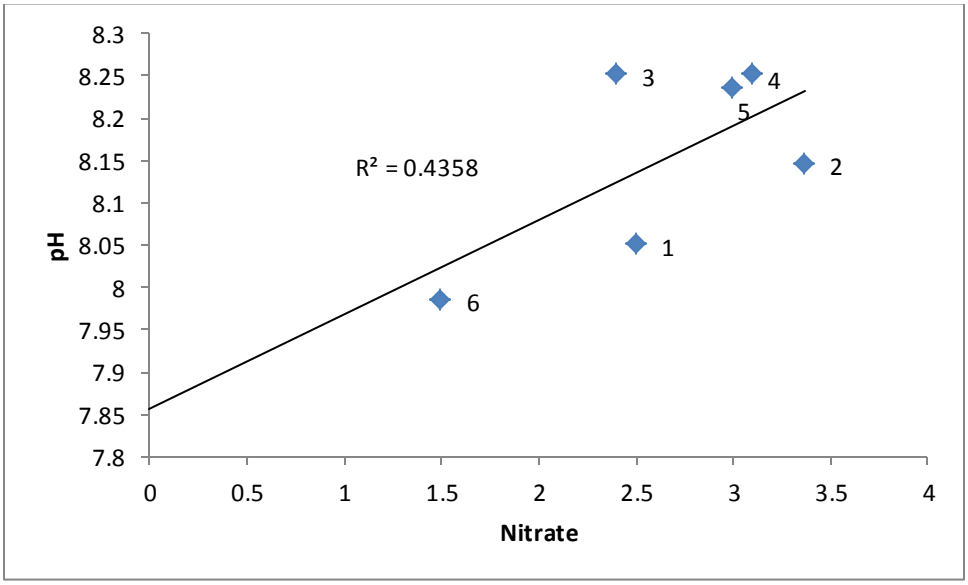


Figure 4.11 Correlation between median pH values and median nitrate concentrations in the catchments.

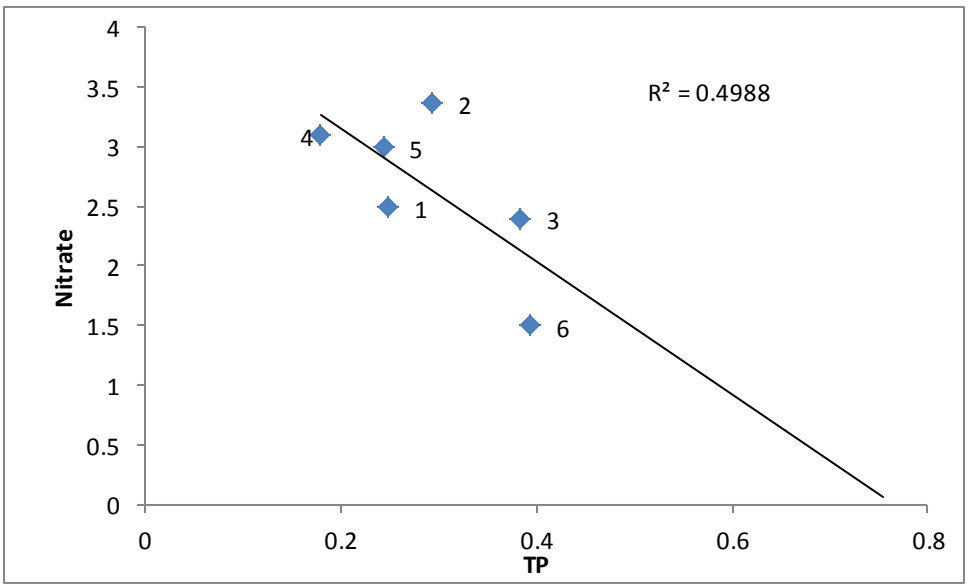


Figure 4.12 Correlation between median total phosphate concentrations and nitrate concentrations in the catchments.

Since urban area has lower nitrate concentration, it would have less photosynthesis and hence, the pH will be lower and therefore has a negative correlation in urban areas. It can be concluded that LULC and soils affects nitrate and TP in the rivers, while photosynthesis is the underlying reasons for the correlations among nitrate, TP and DO. There is a moderate negative correlation (R^2= -0.5) (Figure 4.12) between TP and nitrate. Hydrogen ions are consumed during the process of photosynthesis, therefore increasing the pH levels. Hence, a moderate but positive trend (R^2= 0.46) (Figure 4.11) between pH and Nitrate could be seen.

Turbidity is directly related to concentrations of Total Phosphate (TP) (Table 4.4). There is a moderate but positive trend between TP levels and turbidity (R^2= 0.61) which could be due to attachment of phosphate to suspended particles in the water. A moderate negative trend (R^2=-0.50) could be seen between DO and Turbidity. This trend may indicate higher phosphate for photosynthesis.

Water quality variables	**r^2 values based on median values from sampling points within each catchments**	**r^2 values based on all 32 sampling points within the study area**
nitrate vs TP	-0.50	-0.04
pH vs nitrate	0.46	0.21
DO vs nitrate	0.59	0.21
Turbidity vs TP	0.61	0.04
Sp.cond. vs pH	-0.47	-0.06

Table 4.5 Comparative table for Pearsons correlation values.

Although the moderate correlations exist among selected water quality variables (Table 4.4), however, the correlations weaken when all 32 data points are used (table 4.5). It could be that other unidentified factors or processes in each catchment influence the water quality parameters in each catchment.

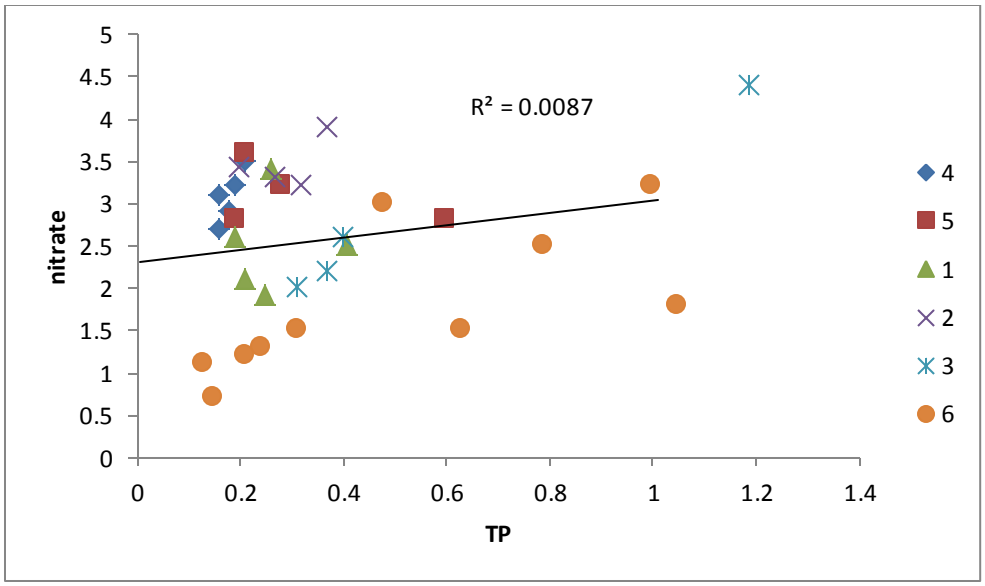


Figure 4.12a Correlation between nitrate and TP for all data points.

For example, the r^2 value for median values for a plot of nitrate vs. TP is -0.50. But, r^2 value for correlation between nitrate and TP for all the 32 points is weakened (Figure 4.12a). Same way Figures 4.12b-4.12e shows the weakened correlation with respect to its median values (Table 4.5) for other water quality variables when all 32 points were considered for correlation.

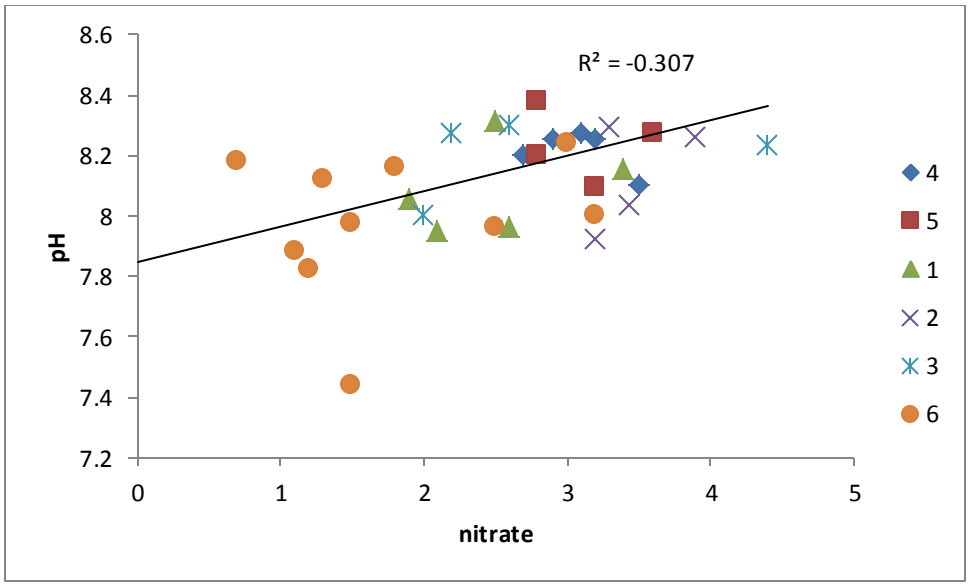


Figure 4.12b Correlation between nitrate and pH for all data points.

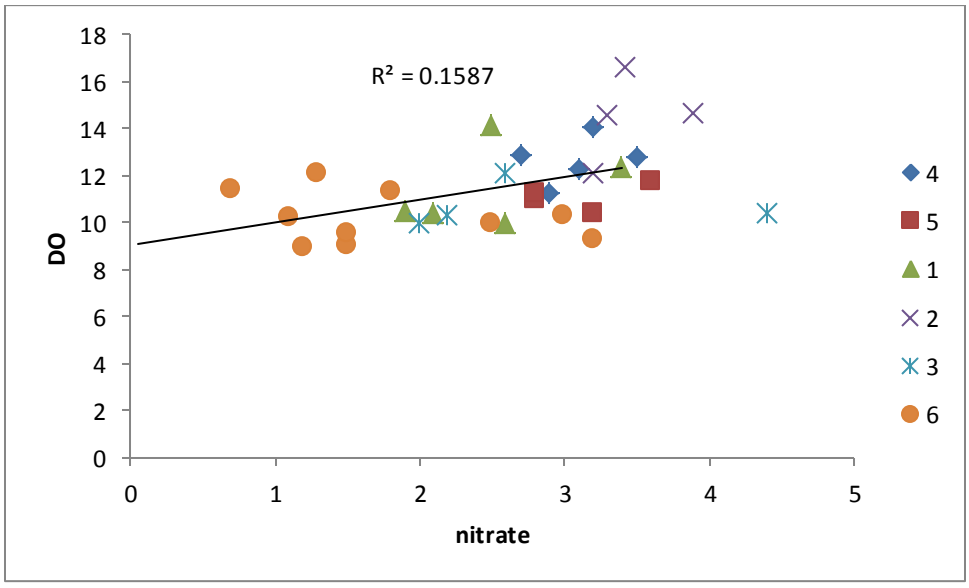


Figure 4.12c Correlation between nitrate and DO for all data points.

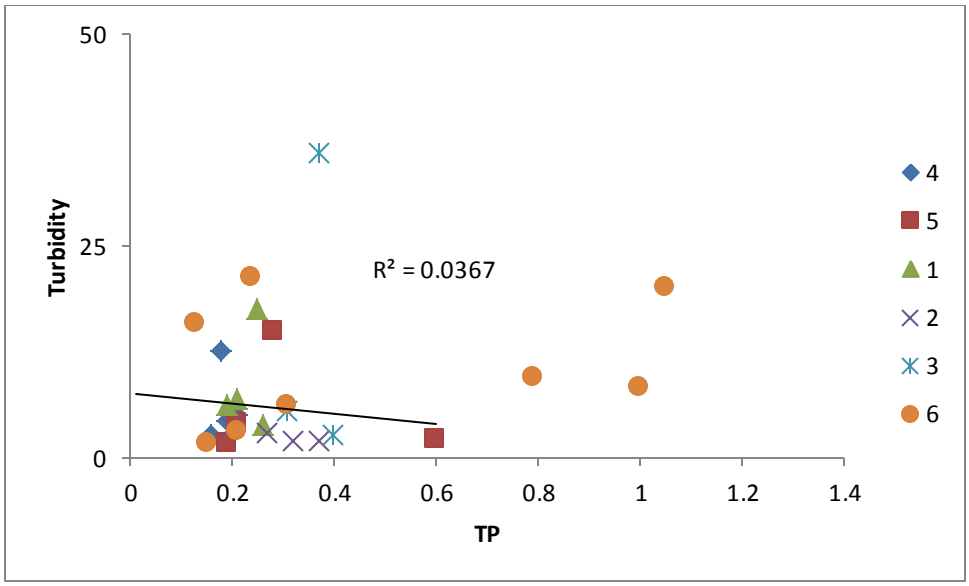


Figure 4.12d Correlation between turbidity and TP for all data points.

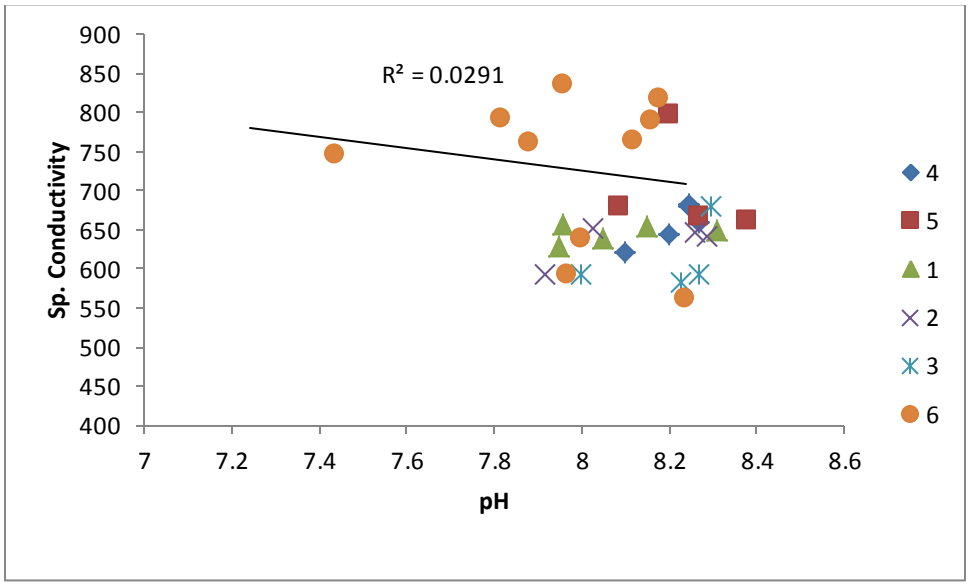


Figure 4.12e Correlation between sp. conductivity and pH for all data points.

4.3 Major Ions

Factors such as geology, soils, LULC influence the water chemistry of the streams within the basin. The study area is located in the calcium carbonate (limestone) terrain. Also, majority of the LULC is agriculture. Soil properties such as drainage, organic matter, adsorption properties etc. play an important role in ion concentrations in the streams.

	K^+	Na^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	SO_4^{-2}
% Agriculture area	-0.22	-0.94	0.32	0.41	0.28	-0.91	0.50
% Urban area	0.15	0.95	-0.23	-0.30	-0.27	0.95	-0.54

Table 4.6 Pearson's correlation matrix for LULC and major ions

Table 4.6 shows the persons correlation matrix for the % urban and agriculture areas correlated with the major ions. Strong positive trends were seen for Na^+ and Cl^- ions with respective to urban areas. This trend is due to the road salt application in urban area. Mg^{2+}, SO_4^{-2} and F^- ions showed moderate positive correlation with % agriculture area. This trend can be related to use of fertilizers in agricultural areas. F ions showed weak but positive correlations with increase in % agriculture area. K^+ ions showed a weak correlation with increase in urban areas. Ca^{2+} showed moderate but positive correlation with increase in % agricultural areas. Since the basin is located on the carbonate terrain, Ca^{2+} ion concentrations in streams could be due to possible bed rock influence.

Figure 4.13 shows that there is a strong correlation (R^2= 0.67) between the percentage urban area and specific conductivity of the water samples in the catchments. One of the reasons for this correlation might be due to fact that the levels of chloride,

sodium and potassium are particularly high in the urban regions and as a result the specific conductivity is giving a strong positive correlation, whereas all other points except for catchment 6 (which is well above other catchment values in Figure 4.17) there is not much of the correlation with Sp. Conductivity.

Similar results were observed in the study of Great Miami River, which showed that increase in the percentage of urban areas had influence on increased levels of specific conductivities, since the water quality shows the cumulative impact of the urban landscape (Wang &Yin, 1997).

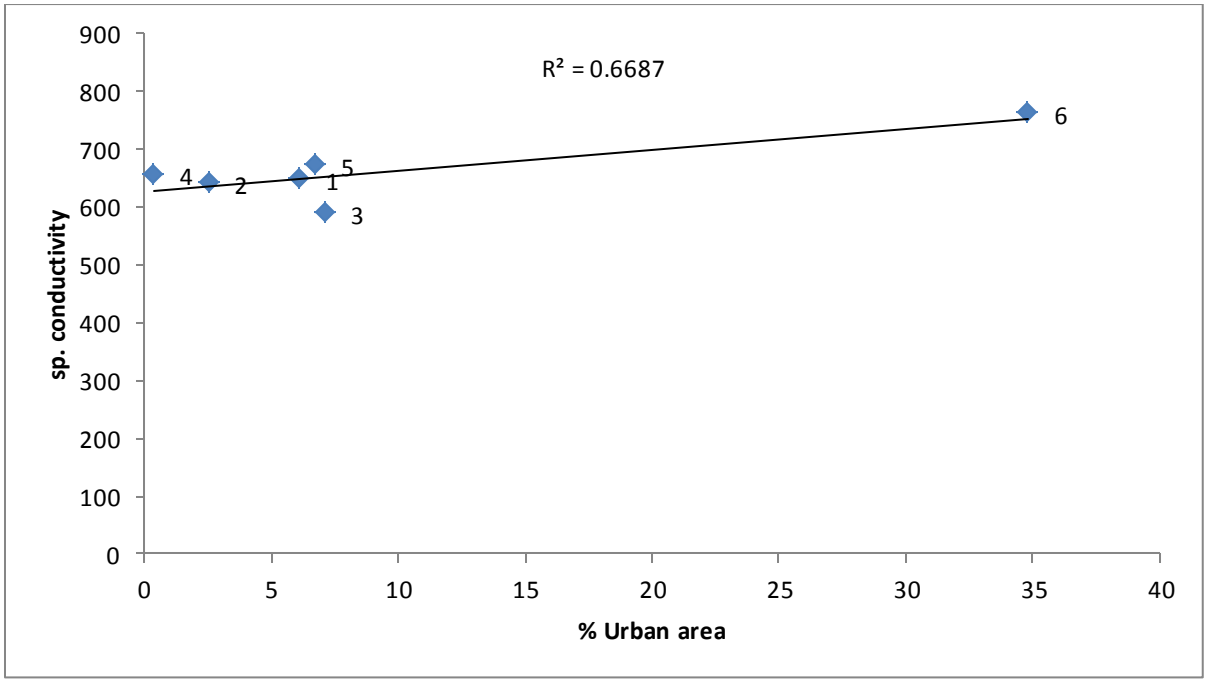


Figure 4.13 Correlation between median specific conductivities and % of urban area in the catchments.

There was negative (R^2= -0.57) correlation between the specific conductivities and the % agricultural area (Figure 4.14). The correlation here could be misleading due to one particular value (catchment 6). This one value dictates the overall trend line and

elimination of catchment 6 would result in a positive slope. However, overall negative correlation is consistent with a study on Great Miami River (Wang & Yin, 1997).

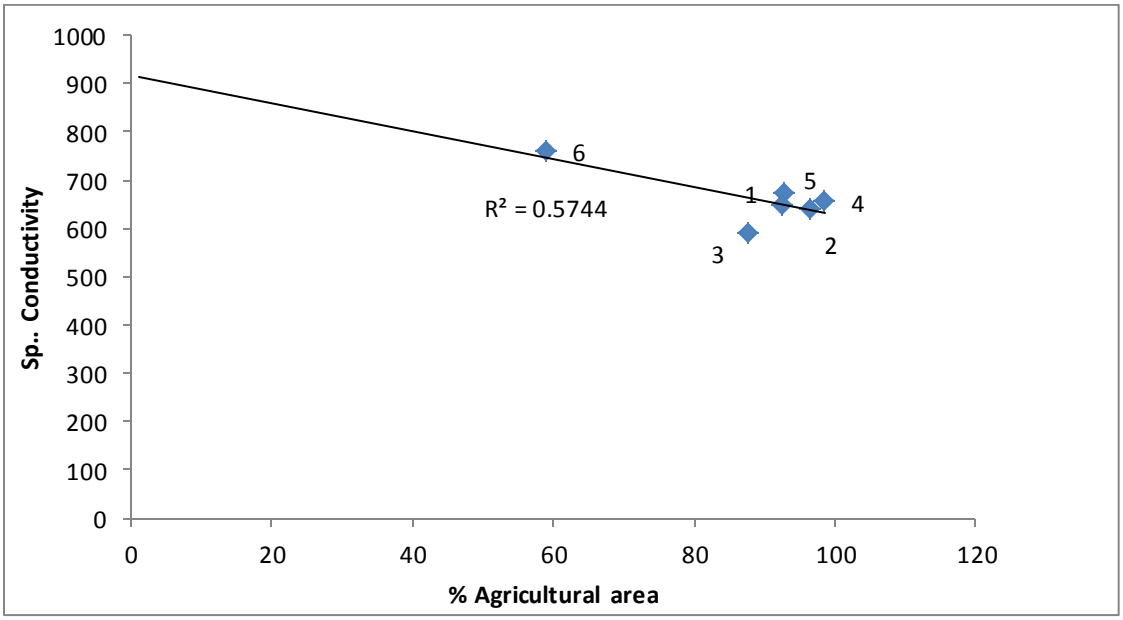


Figure 4.14 Correlation between median specific conductivities and % of agriculture area in the catchments.

In Figure 4.15, Catchment 6 which has the highest percentage of urban land has much higher Na^+ and Cl^- concentrations than other catchments (Table 4.7). The application of road salt in densely populated urban areas is the main source of Na^+ and Cl^-. Figure 4.15 shows that the mean concentrations of sodium and potassium in the streams of the catchment 6.The concentrations of sodium are well above the mean values of the entire study area. High K^+ concentration in catchment 3 can't be explained by using LULC or soil properties. Although both catchments 3 and 6 have high urban %, but not all catchments with high urban %, such as catchments 1(6.17%) and 5 (6.77%) have

high K^+ concentrations (Figure 4.16). Further study would be needed to find out the reason(s) for the high K^+ concentration in catchment 3.

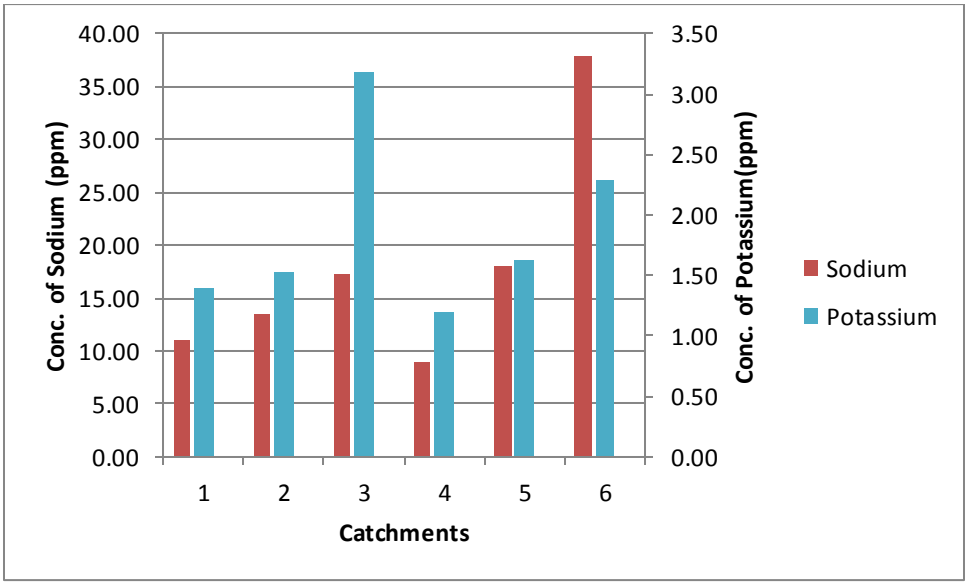


Figure 4.15 Mean concentrations of Sodium and Potassium ions in each catchment.

Catchment	Na^+ ppm	K^+ ppm	Mg^{2+} ppm	Ca^{2+} ppm	F^- ppm	Cl^- ppm	SO_4^- ppm
1	10.95	1.40	29.82	72.36	2.14	23.60	40.33
2	13.40	1.53	31.00	68.80	3.73	22.69	36.30
3	17.26	3.19	19.59	47.61	1.84	23.52	42.32
4	8.88	1.20	32.12	71.85	2.67	21.60	56.51
5	17.95	1.63	32.80	72.51	1.82	34.99	34.59
6	37.89	2.29	22.75	56.24	1.73	76.10	25.95

Table 4.7 Mean concentration of major ions in each of the catchment areas

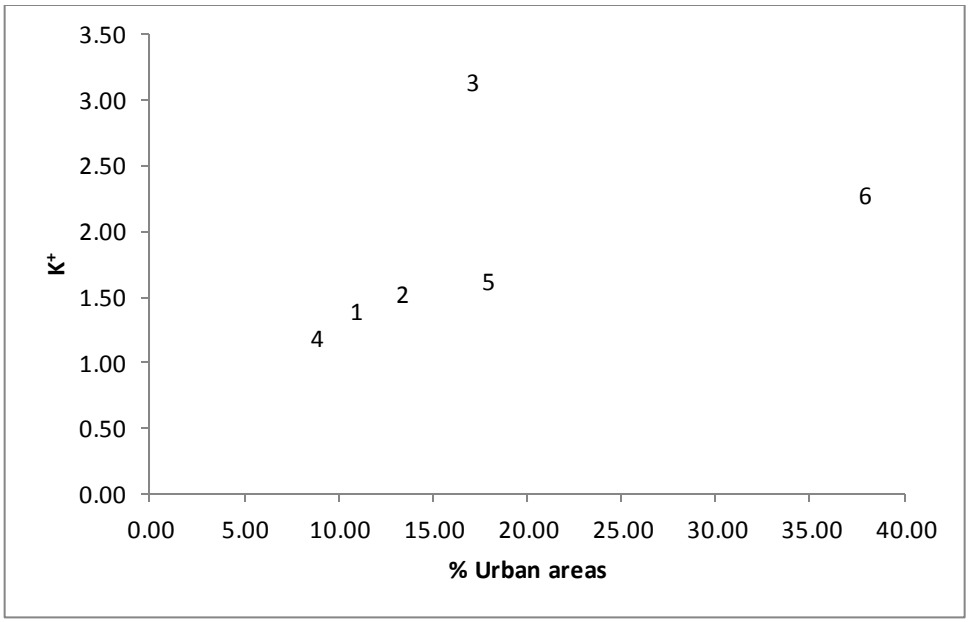


Figure 4.16 Trend of concentrations of potassium ion with % urban areas.

Figure 4.17 shows that the K^+ concentration is typically proportional to the Na^+ concentration, with the exception of catchment 3. Higher Na^+ concentration could leach adsorbed K^+ ions and increase the K^+ concentration in stream water.

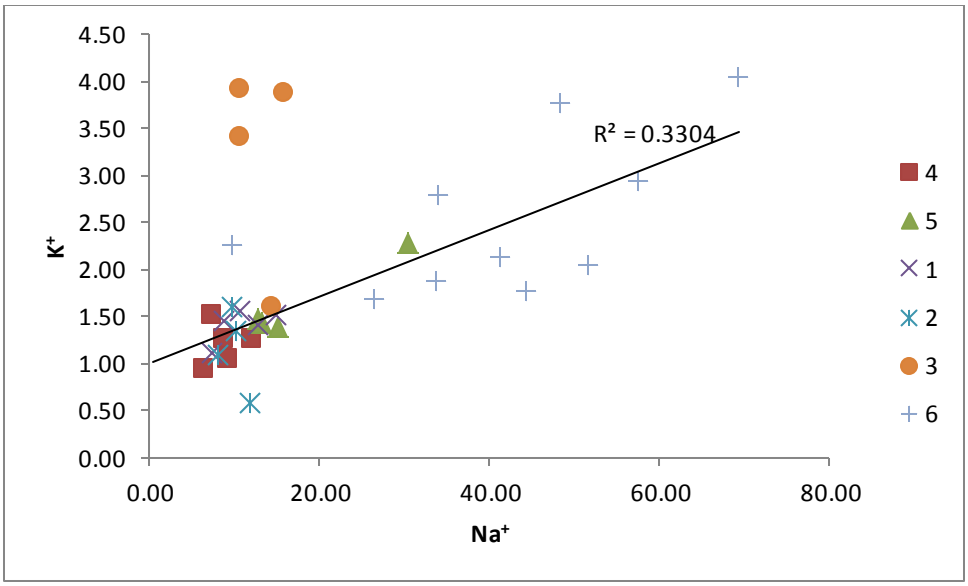


Figure 4.17 Trend of sodium and potassium concentrations in sampling points.

Figure 4.18 shows the trend for calcium and magnesium ions. There is a strong positive correlation between these two ions. The study site is located within a carbonate terrain. It would be expected to have Mg-Ca-HCO_3^- type water. Catchment 3 and catchment 6 have much high sodium and potassium levels, but lower in Magnesium and calcium concentrations. Saturation indices of calcite for samples (Appendix D) were in the range of -0.12 to 0.75 which shows that most stream waters are in equilibrium or oversaturated with calcite and the soil.

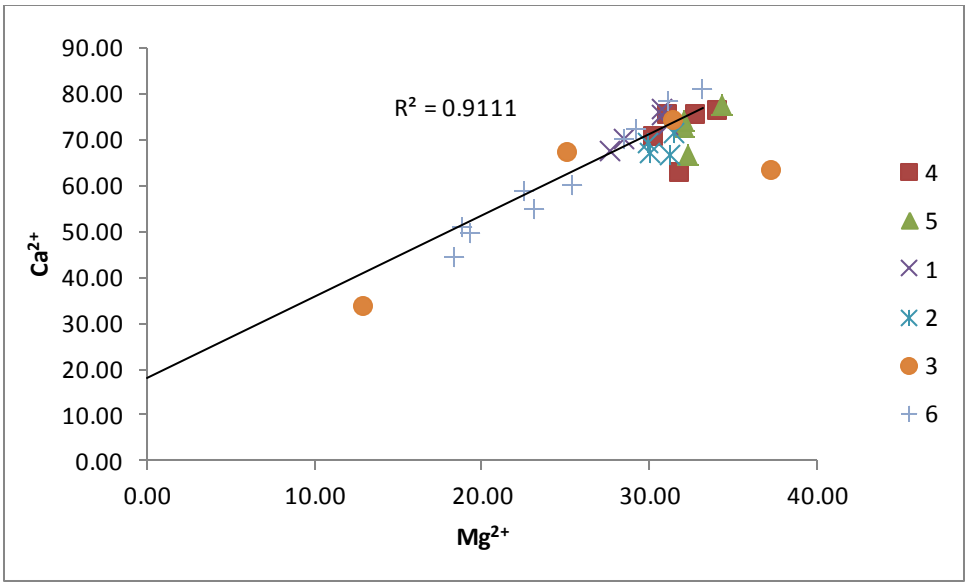


Figure 4.18 Trend for calcium and magnesium concentrations.

Based on the mean concentrations of chloride, sulfate and fluoride concentrations from the table the mean chloride concentrations of the samples obtained from streams of the catchment 6 is at about 76.10 ppm which is way higher than the overall mean at 40.99 ppm. Sulfate ion concentration is more evenly distributed amongst the streams in the catchments from 2-5 apart from catchment 1 and 6. The mean fluoride ion concentration for the streams in the overall study area is at 2.22 ppm with the exception of catchment 4, where the mean concentration is at 3.73 ppm. High Fluoride levels may be due to the runoff from fertilizers used in the agricultural areas.

Figure 4.19 shows the positive but moderate trend for sulfate and fluoride concentrations in the water samples. The concentrations of these ions are proportional to each other and both of these ions increased with increasing % agricultural areas.

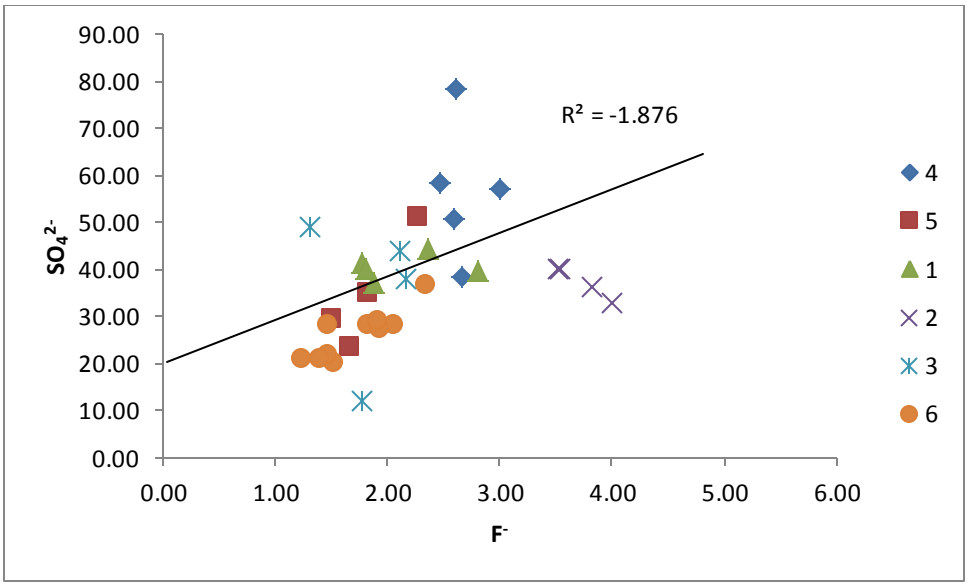


Figure 4.19 Trend for sulfate and fluoride concentrations.

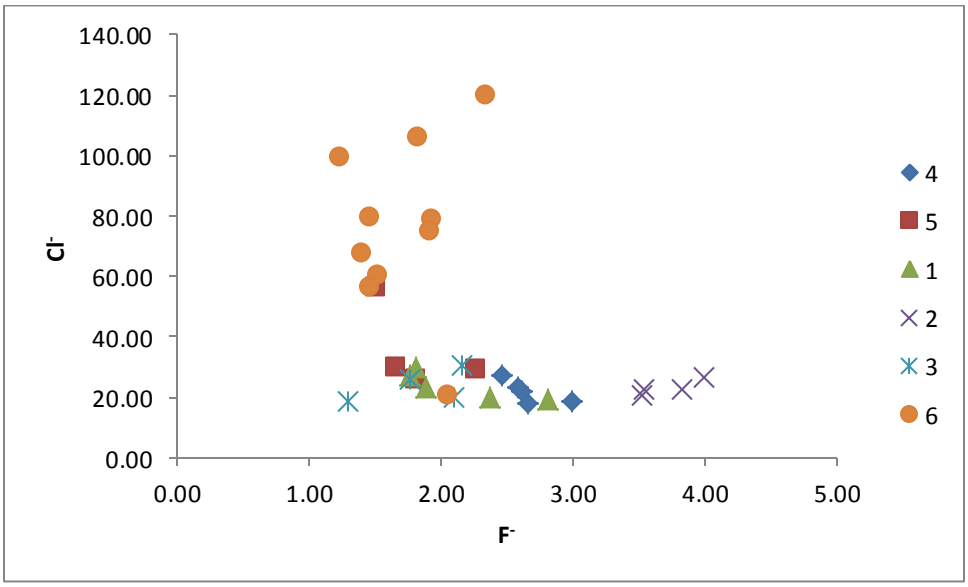


Figure 4.20 Trend for chloride and fluoride concentrations.

Each catchment may have its own unique processes or factors that influence the correlations among solutes. For potassium- sodium plot (Figure 4.17), samples from catchment 3 do not follow the general trend. In Figure 4.20, the relationship between chloride and fluoride in catchment 6 is quite different than the other catchments. Further investigations would be needed to find out the cause(s) for those deviations.

4.3.1 Mineral Stability and Water Chemistry

Because of low solubility of aluminum, dissolution of aluminosilicates, such as kaolinite, and feldspar typically causes precipitation of secondary minerals. Since solubility of Al is in the low µg/L level, it is assumed aluminum to be conservative, i.e., aluminum released from one aluminosilicate will be incorporated into the secondary solid phase. For example, incongruent dissolution of K-feldspar to kaolinite is expressed as:

$$2KAlSi_3O_8 + 2H^+ + 9H_2O \leftrightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 4H_4SiO_4 \qquad (6)$$

Eq. (6) is a linear equation when plotted on log (a_{K^+}/a_{H^+}) vs. log (a_{H4SiO4}) diagram, and it represents a stability phase boundary between k-feldspar and kaolinite.

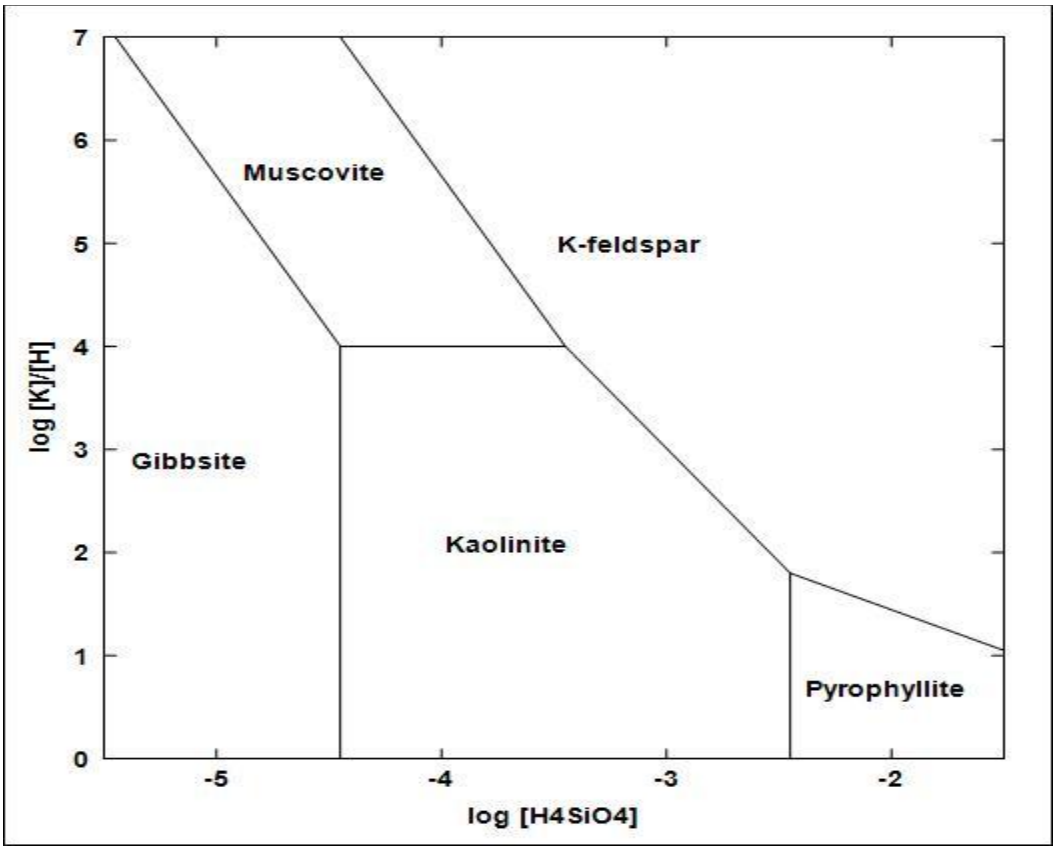
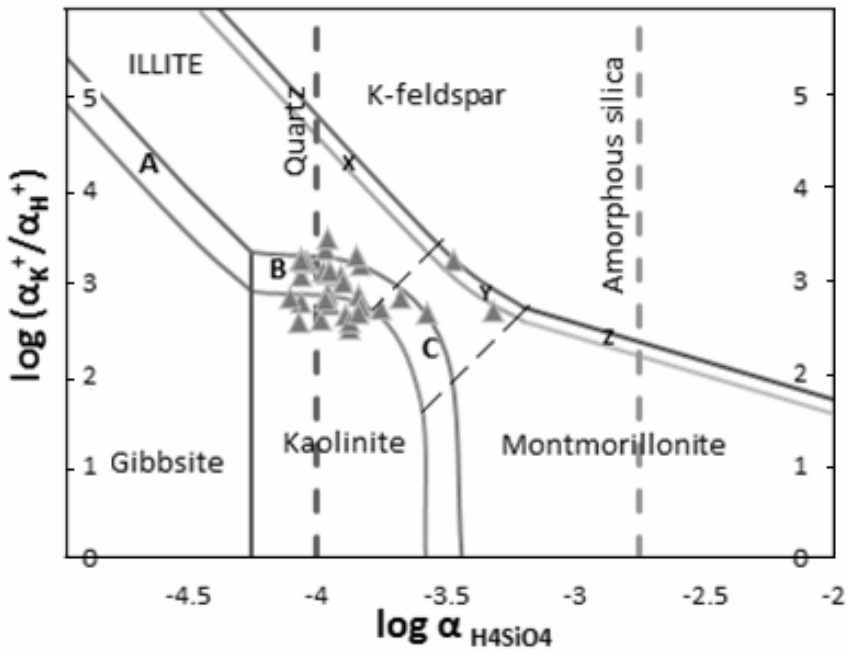
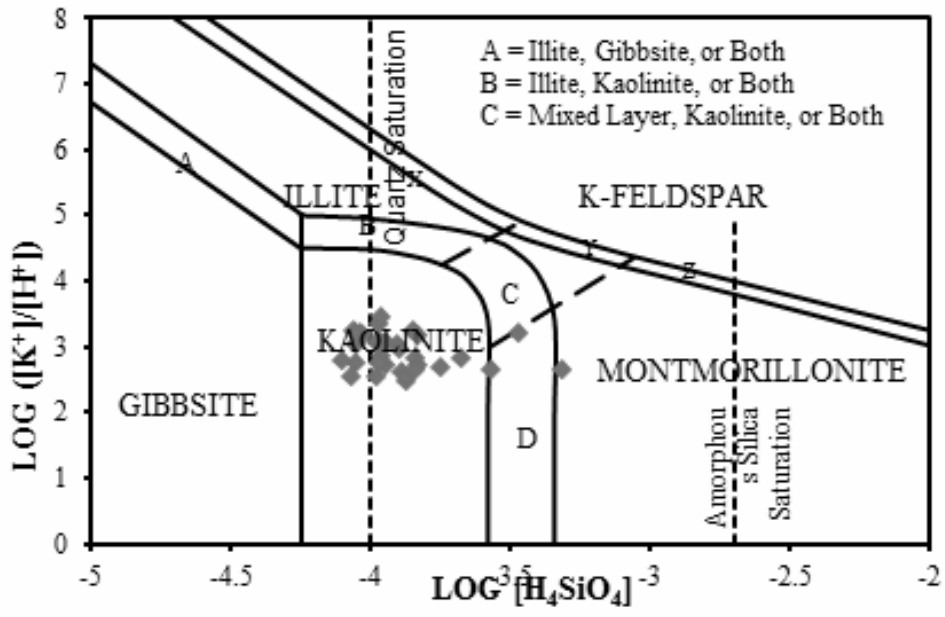


Figure 4.21 Silica stability diagram for K_2O-H_2O-SiO_2-Al_2O_3 system.



a) Ordered $2M_1$ muscovite component



b) Disordered $1M_d$ muscovite component.

Figure 4.22 Stability relationships amongst minerals in K_2O-H_2O-SiO_2-Al_2O_3 compositions of water collected from the outlets of each catchment in the study area superimposed on the graph a) ordered $2M_1$ muscovite component b) Disordered $1M_d$ muscovite component (after Aagard et al., 1983).

Figure 4.21 is a mineral stability diagram in the K_2O-H_2O-SiO_2-Al_2O_3 system, where muscovite and pyrophyllite are stable phases. However, illite and montmorillonite are more common in soil. Gibbsite, kaolinite, illite and vermiculite have been identified in this region (Huang, 1992). Illite, not muscovite, is one of the clay minerals that influence water chemistry in LMRB. Mineral stability diagrams that include illite and other mixed layer clay minerals are likely the better representations of the local soil-water system.

Aagard et al., (1983) constructed two such diagrams for K_2O-H_2O-SiO_2-Al_2O_3 system, one with ordered illite and the other with disordered illite (Figure 4.22). All the data points are superimposed on the diagram (Figure 4.22). It can be noticed that almost all points are located near the illite-kaolinite boundary (Figure 4.22(a)) or within the kaolinite field (Figure 4.22(b)). Even though the orderness of illite in this region has not been studied, illite is a common clay type in this region. Figure 4.22(a) seems to represent the soil-water stability relationship better.

Figure 4.23 is a mineral stability diagram of the CaO-SiO_2-H_2O-Al_2O_3 system constructed based on the same principle of incongruent dissolution. All the samples collected from sampling outlets showed that the mineral equilibrium amongst in the water was found to be near the kaolinite-Ca-beidellite boundary.

Ca-beidellite was not identified by Huang, (1992). Instead, vermiculite was identified. However, reliable thermodynamic data for vermiculite do not exist, vermiculite could have similar stability relationship similar to beidellite if ($a_{mg}^{2+}/a_{H^+}^{2}$)

ratio is high (Drever, 1999, page 271). The ($a_{mg}^{2+}/a^2_{H^+}$) ratios of the samples range from 10 to 12 and it is reasonable to assume vermiculite is the clay that occupies the stability field of beidellite of Figure 4.23. Further study is needed to identify the Ca- bearing 2:1 clay that influences water chemistry in this system.

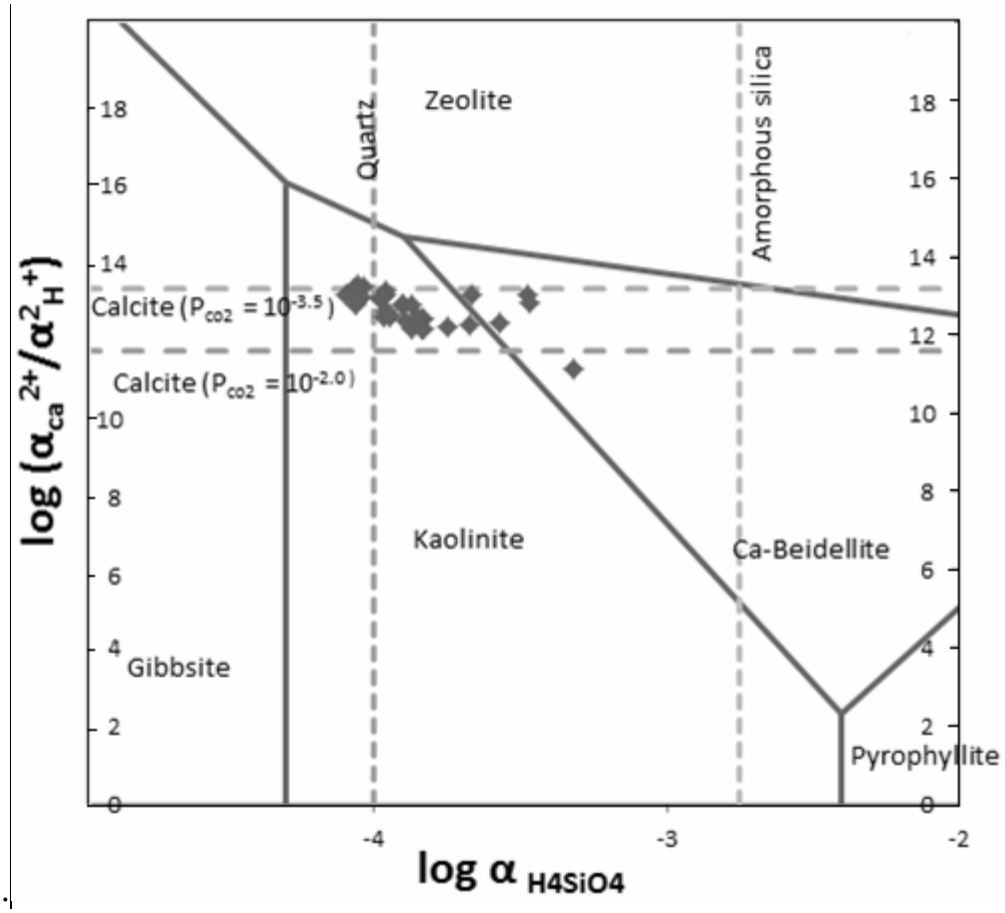


Figure 4.23 Stability relationships among some minerals in the CaO-SiO_2-H_2O-Al_2O_3 system at 25° C with the compositions of water collected from the outlets of each catchment in the study area superimposed on the graph. (after Drever, 1997).

The horizontal dashed line represents the saturation values of calcite under partial pressure of CO_2 gas (pCO_2) of atmosphere $10^{-3.5}$ and of soil atmosphere $10^{-2.0}$ respectively. Local ground waters have a theoretical equilibrium pCO_2 of $10^{-2.0}$ and the

pCO_2 of atmosphere is at $10^{-3.5}$ atm. All points fall on calcite-equilibrium line at pCO_2 of $10^{-3.5}$atm, which is the pCO_2 in the atmosphere. Samples were collected during dry season and there was no rain prior to the sampling. The discharge of groundwater into the river will gradually move towards the equilibrium with the atmosphere. Majority of sample points fall between those two calcite-saturation lines. It is concluded that equilibrium with calcite under the influence of CO_2 is an important process that affect water the water chemistry in the upper LMRB.

4.4 Impact of LULC on water quality

This section is about production coefficients that were calculated using linear least square regression method for nutrient and major ions for the study area. Table 4.8 summarizes the production coefficients for nutrient.

LULC type	**Phosphate (mg\L\acreage percent)**	**Nitrate (mg\L\acreage percent)**
Urban area	0.036	0.009
Agriculture area	0.004	0.033
Forest area	0.032	-0.04
Others	-0.312	-0.037

Table 4.8 Nutrient production coefficient for the entire study area based on samples from the catchment outlets.

Phosphate production coefficient per acre percentage was at 0.036 mg/L for the urban land scape is significantly high as compared to the other two types of land use. Similar trend was observed by other previous studies (Soranno et al., 1996; Oguchi et al.,

2000; Borchelt, 2007; Brett et al, 2005; Chang, 2008). The reason for high phosphates could be due to soil properties. There are certain observations that have been made relating soils with phosphate concentrations for the study area (section 4.5).

Also, Agriculture area as suggested by the results clearly produced greater amount of nitrate per acre percentage of agricultural land. But, interestingly the forest has a negative nutrient production coefficient for nitrate at -0.04 mg/L per acre percent suggesting that it could be a sink. At the same time, phosphate production coefficient for forest was higher. This trend may be due to the soil properties. Most of the forest (93%) in the study areas is located in catchment 3 and 6. These two catchments happen to be better drained areas of all catchments. More reasoning on high phosphate concentrations are summarized in section 4.5

The fourth group which has high negative coefficient values for nutrient, these values have high uncertainty and their contributions overall are very minimum because of their very less percentage area.

LULC	**Na^+**	**K^+**	**Mg^{2+}**	**Ca^{2+}**
	(mg\L\acreage percent)			
Urban area	2.042	0.013	0.168	0.444
Agriculture area	0.187	0.019	0.209	0.764
Forest area	1.016	0.531	-4.255	-1.516
Others	-15.717	-0.478	10.947	-2.212

Table 4.9 Production coefficients for cations in the study area.

Calcium and magnesium ions were produced in greater amounts by agricultural areas when compared to urban areas (Table 4.9). The study site is located in a carbonate terrain rich in calcium and magnesium. Koc et al., (2008) found that levels of ions in the streams close to agriculture areas depend on the drainage systems, the intensity of farming operations, and also the availability of riparian buffers. Based on his observations soil drainage could also have played a role in upload of solutes in the streams.

The production coefficients Na^+, Cl^- was also found be greater for the urban areas (Table 4.9 and 4.10). This might be due to use of road salts especially in urban areas. This kind of trend was found in a previous study where the surface waters of the Grand Traverse Basin in Michigan (Wayland et al., 2003).

LULC	**SO_4^{-2}**	**Cl^-**	**F^-**	**SiO_2**
	(mg\L\acreage percent)			
Urban area	0.378	3.857	0.009	0.059
Agriculture area	0.561	0.360	0.024	0.089
Forest area	-7.374	1.356	-0.014	1.793
Others	7.442	-3.576	-0.017	-1.639

Table 4.10 Production coefficient for anions and silica in the study area

Ions such as sulfate and fluorides to some extent were produced more by the agricultural lands compared to urban areas (Table 4.10). The reason could be due to farming activities, which could enhance weathering and oxidation of sulfide. Based on production coefficients, forests are seen to be acting as a sink for sulfates and source of silica and chloride. More detailed study is needed to understand the reason(s) of the forests behavior.

The reason for the high positive or negative production coefficients for the "Others" group could be because of high uncertainty associated with its very small area. Its overall contribution is very small.

4.5 The Impact of soil on N and P.

Soils play a vital role in affecting water quality of rivers in a basin. Erosion of soil is one of the key problems associated stream water quality. Soils are naturally formed by weathering of rocks and minerals. They tend to have various components including clay minerals, ions, organic matter, phosphates, rock fragments etc. Most sediment in the surface waters of the rivers are derived from eroded top soils. The naturally formed phosphates are found attached to the soil particles. The eroded sediments increase turbidity of the river water.

Soil properties, including, texture, organic matter content, and runoff potential etc., could affect water quality through soil-water interactions, such as dissolution and precipitation of mineral and ion exchange soil and water. Soil maps from NRCS website contain properties of soil and the distribution of soil types. Figure 4.24, shows the property of soil drainage map for the study area. Most of the catchment 2 is poorly

drained but this region is characterized by absence of riparian buffers leading to excessive nitrate in these regions (Ohio EPA, 2002).Whereas the catchment 6 contains more soil classified as excessively drained than other catchments (Table 4.11) of the soil map and most of the regions of the catchment 6 is well drained. The phosphate concentrations are high in the streams of this catchment, coincides with production coefficient of excessive drainage areas.

Catchment	% of poorly drained land	% of moderately drained land	% of well drained land	% of excessively drained land
1	54.27	5.84	36.67	3.22
2	62.32	5.33	26.06	6.31
3	22.43	4.27	60.78	12.52
4	78.75	6.26	10.39	4.60
5	18.23	7.86	21.63	11.26
6	15.28	2.32	63.77	18.71

Table 4.11 Zonal Statistics data for drainage in the study area.

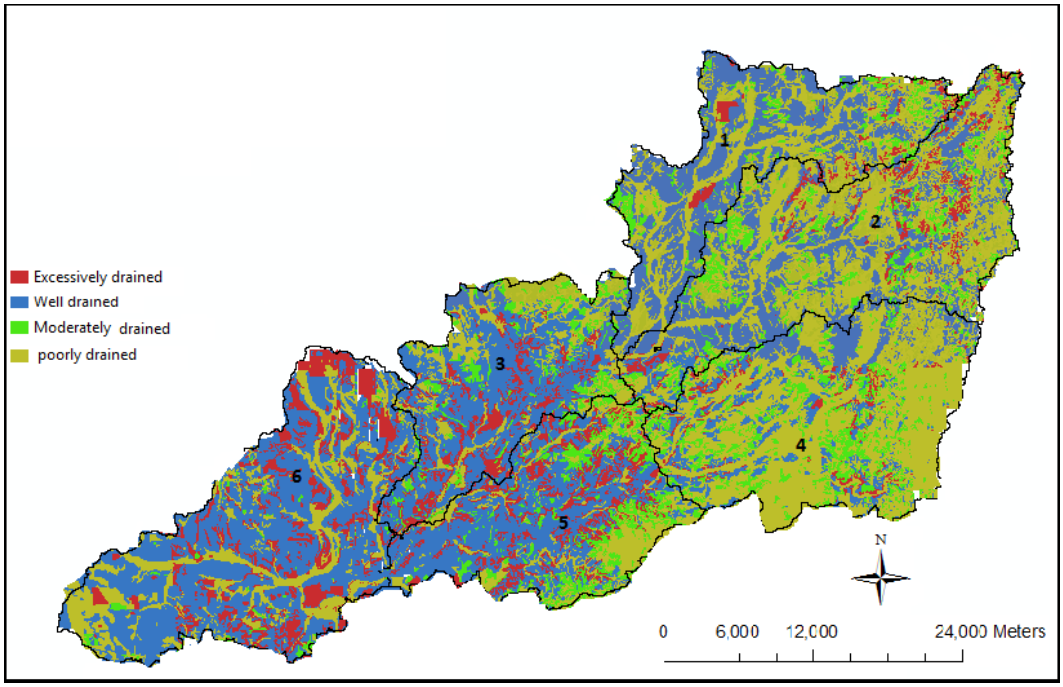


Figure 4.24 Soil map depicting the drainage scale of the study area

Least square linear regression method was used to find the production coefficients for nitrate and TP for the drainage map and the results are summarized in table 4.12. It shows that the areas with excessive drainage have higher production of TP; other drainage categories do not seem to produce much TP. Excessively drained soil should produce more eroded soil particles. If the phosphate ions are attached to the soil particles, it could be expected to produce more TP in the water. On the other hand, drainage pattern on nitrate production doesn't show a clear pattern. This trend maybe because, nitrate is readily soluble.

Drainage type	**Production coefficient mg/L/acreage percent**	
	Nitrate	**TP**
Poorly drained area	0.025	0.001
Moderately drained	0.176	-0.006
Well drained area	-0.010	-0.002
Excessively drained area	0.105	0.059

Table 4.12 Production coefficients for Total Phosphate (TP) and nitrate for different drainage patterns across the study area.

Organic matter (OM) is a product of decay of organic compounds or living organisms and they hold rich nutrient essential for plant growth. Interestingly, OM in the urban soils in this study area is greater when compared to the other areas. The percentage of OM is ranging from 2-5.5 percent (Figure 4.25) of the urban soils, mainly around the Beavercreek area in catchment 6 and around yellow springs in catchment 3. Table 4.13 shows the distribution of OM in soils and its distribution across the study area. Also, Figure 4.26 shows the map with the distribution of organic matter. The percentage OM in soil of the catchments 3 and 6 had higher mean percentage of OM in soils. Incidentally, they are also the most urbanized part of the study area.

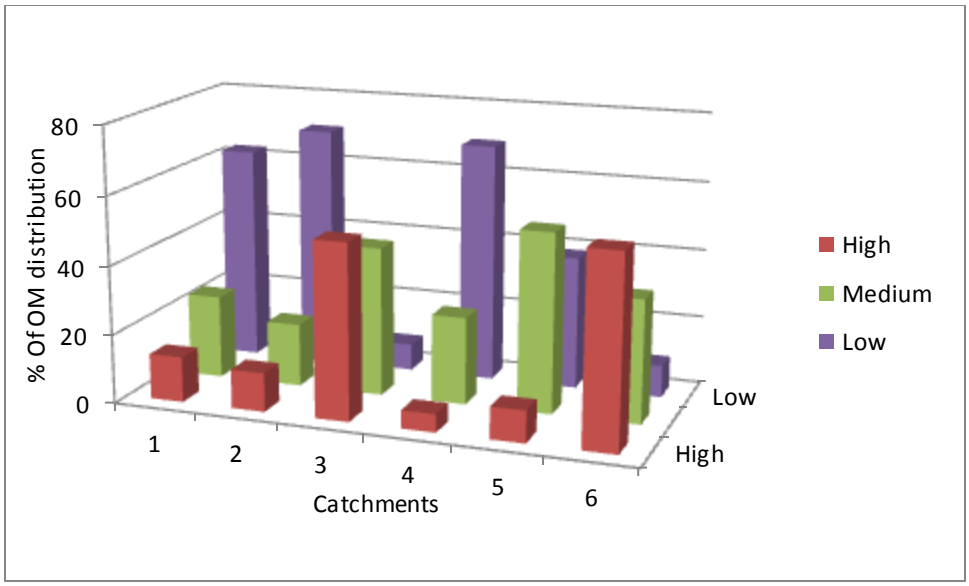


Figure 4.25 Organic Matter distributions across different catchments with the values are classified into high content (3%-4.5% OM), medium content (1%-3% OM) and low content (0.1%-1% OM)

Catchment	Range of soil Organic Matter content %	% of high OM content soil	% of medium OM content soil	% of low OM content soil	Mean OM %
1	0.2- 4.5	13.18	24.17	62.65	1.20
2	0.2- 4.5	11.27	18.30	70.43	1.08
3	0.1- 5.5	50.93	43.21	7.72	2.60
4	0.2- 4.5	5.26	25.36	69.38	0.95
5	0.2- 4.5	9.27	52.08	38.65	1.34
6	0.1- 5.5	55.14	35.62	9.24	2.65

Table 4.13 Zonal statistics of organic matter distribution in soils of the study area.The values are classified into high content (3% - 4.5%), medium content (1%-3%) and low content (0.1%- 1%).

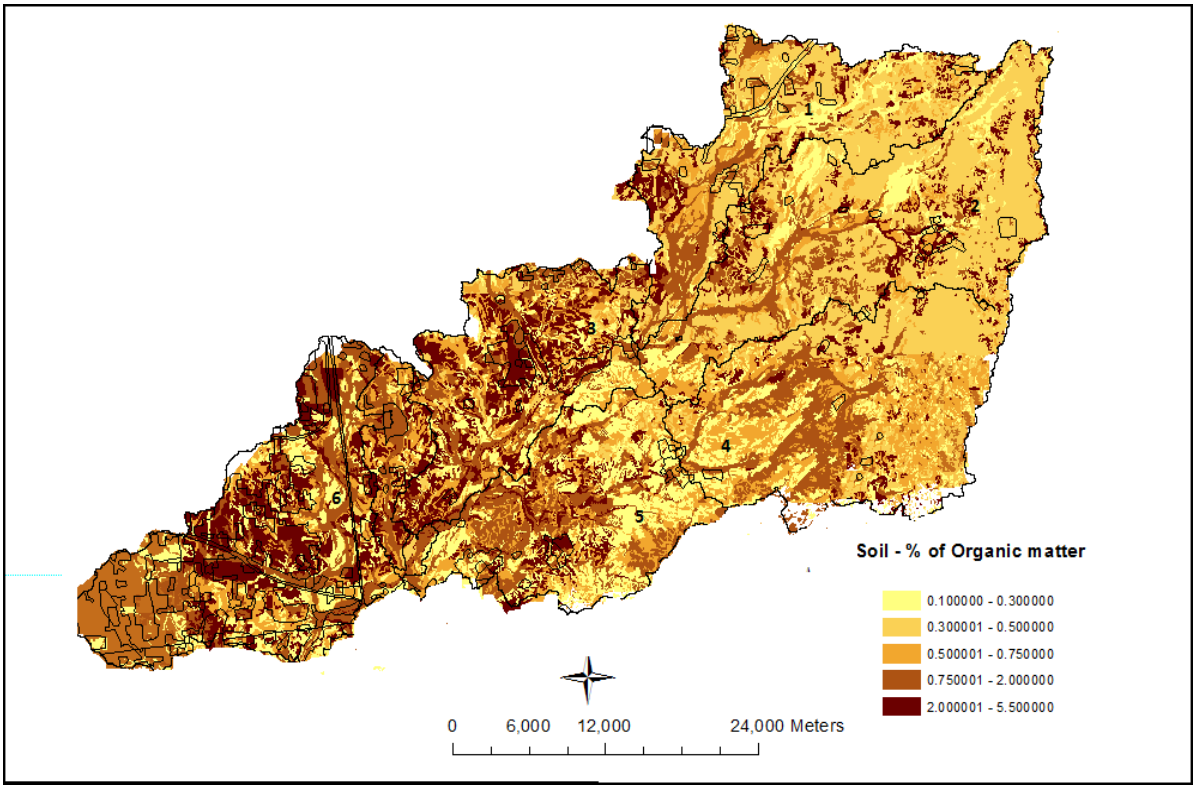


Figure 4.26 Map of the study area showing organic matter distribution.

Figure 4.27 and 4.28 show the trend for TP and nitrate against % OM in soil. There is a positive trend between OM concentrations and TP levels. This trend coincides with urban areas where greater TP trends were seen.

Moderately negative correlation was seen between nitrate and OM percentage in soils of the water samples collected at the catchment outlets. At this point it is not clear whether the TP concentrations are due to OM in soils or due to the urbanized areas. As seen before there is an inverse relationship between TP and nitrate, with OM showing inverse relationship with nitrate as well.

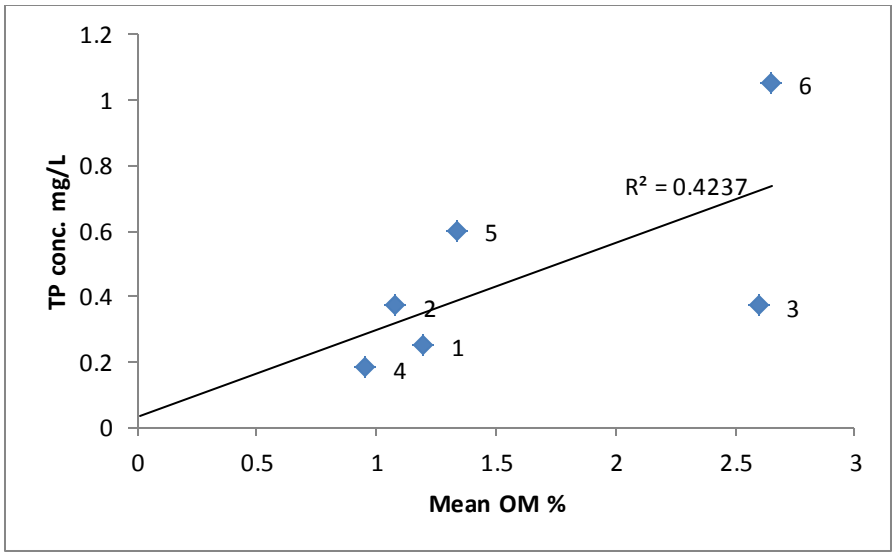


Figure 4.27 Trend of soil OM distribution with respect to median TP concentrations in the study area.

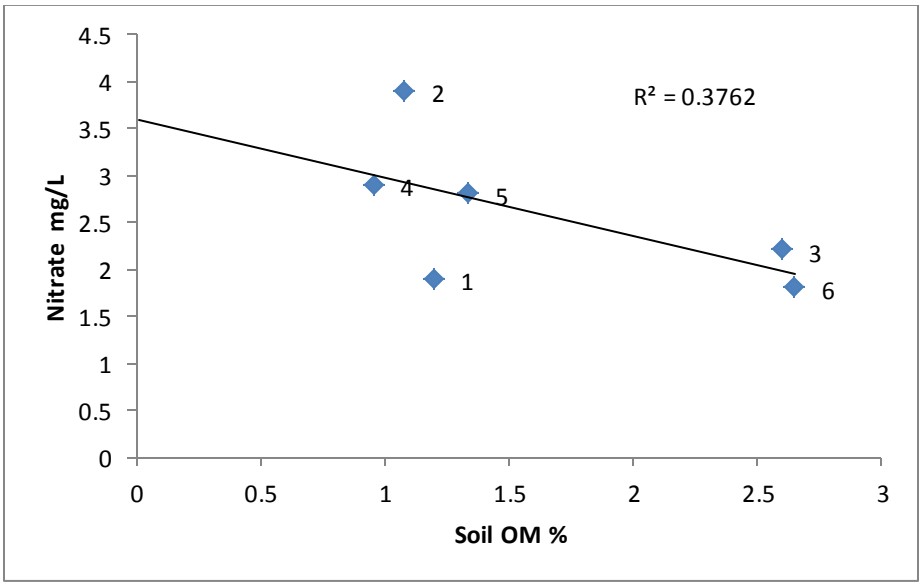


Figure 4.28 Trend of soil OM distribution with respect to median nitrate concentrations in the study area.

Based on the above analyses, Table 4.14 shows the summary of phosphate, Soil OM, Urban area percentage and drainage.

Catchment	TP (as PO_4^{-3}) mg/L	% Urban area	Mean % Soil OM	% Well drained area	% Excessively drained area
1	0.26	6.17	1.2	36.7	3.2
2	0.29	2.57	1.08	26.1	6.3
3	0.57	7.15	2.6	60.8	12.52
4	0.18	0.42	0.95	10.4	4.6
5	0.32	6.77	1.34	21.6	11.3
6	0.55	34.82	2.65	63.8	18.7

Table 4.14 Summary of phosphate, Soil OM, Urban percentage and Drainage

Catchments 1, 3 and 5 have about the same % of urban area, but catchment 3 has much higher TP. Although catchment 6 contains much high % urban area, its TP is about the same as catchment 3. High TP in catchments 3 and 6 are associated with high OM and well-drained soil. It can be concluded that TP is clearly related to the soil OM and drainage property, rather than urbanization.

5.0 SUMMARY AND CONCLUSIONS

It is assumed that stream water quality is a cumulative result of leaching of various land surfaces by precipitation. The purpose of the study is to estimate the effect of LULC and soil on water quality. Zonal statistics were used to estimate the percentage area of various LULCs and soil properties. Production coefficients of each LULC and soil properties were estimated using least square linear matrix operation.

The study area of the upper Little Miami River Basin (LMRB) is vastly dominated by the agricultural land use. Important streams that drain this part of the basin are the Massies creek, Beaver Creek, and north fork Little Miami. The study area was delineated into 6 catchments with ArcGIS and BASINS. All the catchments are predominantly agriculture land use except catchment 6 which encompasses the Beavercreek area. This catchment had the greatest percentage of urban land use compared to the others.

Based on all the analysis the following observations were made.

1) Phosphate production coefficient for the urban areas was significantly greater. The Beavercreek and Little Beaver creek carried greater amount of phosphates as compared to the other streams of the basin. However, it was found that high

phosphate concentrations are associated with better drained areas and soil organic matter. Urbanization doesn't seem to be the factor.

2) Nitrate production coefficient was greater for agricultural land. Nitrate levels were significantly higher in the Massies creek, north fork Little Miami due to agricultural runoff
3) Strong trend of chlorides and sodium were observed with increase in the percentage of urban land use which may be due to the road salts. The production coefficients for these ions were also significantly greater,
4) Magnesium, calcium and sulfates showed positive and strong correlation with increase in the percentage of agriculture area, likely due to disturbance of soil during farming activities.
5) Mineral equilibrium indicates that illite and kaolinite are the dominant clay minerals that influence the potassium and silica concentration. Equilibrium with calcite under the partial pressure of atmospheric CO_2 also plays a role in Ca^{2+} concentration.

6.0 FUTURE STUDIES

This study was performed at the area limited to the Upper part of the Little Miami River Basin. By using a smaller area, the correlation between water quality and LULC at a smaller scale can make understanding better. Understandably, the results are limited to a particular type of weather pattern and hydrological condition of that period of time for that limited area. However, continued monitoring and sampling at various periods of time for a bigger basin could give more insight into the relationship between water quality and LULC.

Also, this study was aimed at designing a new method to quantify the amount of nutrient and other solutes in terms of production coefficient that has been exported to the streams and also to find the correlation between land use and water quality. The coefficients of production obtained from this study should be used to evaluate the accuracy of those coefficients to predict stream water quality of different watersheds.

Apart from weather and land use, Point sources such as waste water treatment plant (WWTP) effluents, Industries, Confined feeding operations also impacts the water quality. As an improvement to this project, including point source pollutant data along with NPS pollutants could provide much deeper and better understanding of the watershed systems.

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8.0 APPENDICES

APPENDIX A

FIELD AND LAB DATA

Sampling point no.	DO (mg/L)	pH	ORP	Eh(mv)	Turbidity (NTU)	Chl (µg/L)	Temp (◦C)	Sp. Cond. (µS/cm)
1	12.76	8.10	34.8	234.8	5.0	0.5	21.98	618
2	14.01	8.25	33.9	233.9	4.1	320.0	20.10	678
3	12.27	8.27	34.7	234.7	2.5	1.8	19.70	657
4	12.80	8.20	36.2	236.2	2.2	2.1	22.00	643
5	11.24	8.25	35.2	235.2	12.5	2.2	17.80	681
6	10.97	8.38	35.7	235.7	1.7	1.8	17.28	659
7	11.77	8.27	36.4	236.4	3.9	1.2	19.28	666
8	10.40	8.09	36.4	236.4	14.9	3.6	15.90	677
9	11.25	8.20	36.6	236.6	2.0	1.9	16.70	795
10	14.11	8.31	28.9	228.9	165.0	20.8	19.80	648
11	10.42	8.05	36.0	236.0	17.5	3.3	18.60	637
12	10.40	7.95	36.5	236.5	6.8	2.4	18.60	626
13	9.93	7.96	37.2	237.2	6.1	0.4	18.30	655
14	12.30	8.15	35.1	235.1	3.7	1.5	18.75	653
15	16.57	8.03	39.4	239.4	3.5	0.4	20.84	651
16	12.09	7.92	35.8	235.8	1.9	0.4	20.06	592
17	14.52	8.29	34.9	234.9	2.8	0.6	23.45	639
18	14.58	8.26	36.8	236.8	1.8	1.8	23.72	644
19	12.07	8.30	32.6	232.6	2.6	0.5	20.57	677
20	9.90	8.00	32.6	232.6	5.4	1.2	18.11	590
21	10.40	8.23	30.0	230.0	53.1	5.6	19.31	380
22	10.30	8.27	33.0	233.0	36.0	3.4	20.20	590
23	10.26	8.24	38.2	238.2	275.0	15	19.40	560
24	9.02	7.97	33.1	233.1	74.1	0.4	20.82	592
25	11.32	8.16	36.0	236.0	20.0	4.5	21.40	788
26	12.08	8.12	14.2	214.2	21.3	0.5	20.83	763
27	9.26	8.00	16.5	216.5	8.2	0.5	20.35	636
28	9.97	7.96	53.8	253.8	9.5	0.7	21.22	835
29	9.28	7.82	20.3	220.3	3.1	5.1	20.15	790
30	10.19	7.88	21.9	221.9	15.8	2.5	20.34	761
31	9.52	7.44	23.6	223.6	6.2	1.8	18.20	744
32	11.40	8.18	21.2	221.2	1.6	1.5	17.40	817

Table 8.1 Field data collected using YSI multiprobe sonde on June 21 2011

Sample point no.	TP (mg/L)	PO_4^{-3} (mg/L)	P (mg/L)	NO_3^- (mg/L)	SiO_2 (mg/L)	Alkalinity (mM)
1	0.21	0.28	0.07	3.5	8.6	6.76
2	0.19	0.14	0.06	3.2	7.4	6.94
3	0.16	0.17	0.05	3.1	4.5	5.74
4	0.16	0.08	0.05	2.7	6.7	6.28
5	0.18	0.12	0.06	2.9	5.7	6.92
6	0.19	0.15	0.06	2.8	6.6	5.94
7	0.21	0.16	0.07	3.6	5.4	6.25
8	0.28	0.14	0.09	3.2	9.0	6.55
9	0.60	0.42	0.20	2.8	10.1	6.89
10	0.41	0.17	0.14	2.5	13.5	6.51
11	0.25	0.17	0.08	1.9	7.6	6.28
12	0.21	0.11	0.07	2.1	7.6	6.18
13	0.19	0.10	0.06	2.6	9.2	6.82
14	0.26	0.11	0.09	3.4	20.4	6.94
15	0.20	0.15	0.07	3.4	20.3	6.92
16	0.32	0.18	0.11	3.2	14.6	6.95
17	0.27	0.11	0.09	3.3	10.7	6.96
18	0.37	0.17	0.12	3.9	8.4	6.95
19	0.40	0.24	0.13	2.6	11.1	6.96
20	0.31	0.27	0.10	2.0	12.6	6.94
21	1.19	0.54	0.40	5.4	28.0	5.41
22	0.37	0.34	0.12	2.2	14.0	0.72
23	0.48	0.51	0.16	3.0	13.0	6.97
24	0.63	0.44	0.21	1.5	10.8	6.38
25	1.05	0.31	0.35	1.8	11.4	6.97
26	0.24	0.17	0.08	1.3	13.1	6.40
27	1.00	0.66	0.33	3.2	3.2	4.75
28	0.79	0.49	0.26	2.5	11.1	4.36
29	0.21	0.09	0.07	1.2	2.6	6.85
30	0.13	0.15	0.04	1.1	23.6	6.05
31	0.31	0.16	0.10	1.5	11.3	5.83
32	0.15	0.15	0.05	0.7	7.3	6.79

Table 8.2.1 Lab data- Nutrients, silica and alkalinity concentrations

Sample point no.	Na^+ (ppm)	K^+ (ppm)	Mg^{2+} (ppm)	Ca^{2+} (ppm)	F^- (ppm)	Cl^- (ppm)	SO_4^- (ppm)
1	7.51	1.51	30.36	70.17	2.66	17.95	38.41
2	8.95	1.24	34.18	76.22	2.62	21.66	78.31
3	6.58	0.93	31.90	62.42	3.01	18.13	57.01
4	9.28	1.05	31.26	75.32	2.59	23.23	50.51
5	12.05	1.26	32.89	75.12	2.47	27.03	58.30
6	13.42	1.42	32.44	66.43	2.28	28.87	51.07
7	12.74	1.47	32.12	72.45	1.83	25.60	34.82
8	15.18	1.37	32.22	74.01	1.67	29.53	23.26
9	30.46	2.27	34.41	77.17	1.52	55.95	29.21
10	10.69	1.55	31.22	73.12	1.89	22.86	36.88
11	12.87	1.40	28.56	69.80	1.78	26.75	41.35
12	14.86	1.51	27.69	67.23	1.81	29.44	39.74
13	7.54	1.10	30.82	76.36	2.38	19.99	44.05
14	8.80	1.45	30.81	75.30	2.82	18.95	39.61
15	8.04	1.08	31.62	71.18	3.53	20.10	39.91
16	9.79	1.60	30.06	68.87	3.84	22.32	36.29
17	10.36	1.34	31.31	66.35	4.00	26.19	32.69
18	12.00	0.56	30.13	66.80	3.55	22.18	40.08
19	14.49	1.60	31.60	73.89	2.18	30.05	37.99
20	10.66	3.90	25.26	66.92	1.31	18.53	48.90
21	10.75	3.40	37.42	63.07	1.78	25.95	11.81
22	15.89	3.87	13.06	33.54	2.11	19.54	43.60
23	9.89	2.25	25.51	59.93	2.06	20.22	27.86
24	33.95	2.78	19.38	49.29	1.53	60.43	20.09
25	57.47	2.92	22.62	58.63	1.84	105.67	28.20
26	26.44	1.67	31.15	78.33	1.47	55.85	21.48
27	48.36	3.77	18.36	44.15	1.94	78.63	27.14
28	69.41	4.03	23.16	54.53	2.36	119.97	36.51
29	51.74	2.04	18.93	50.87	1.24	98.99	20.67
30	33.83	1.87	28.54	69.76	1.41	67.21	20.79
31	41.34	2.12	33.28	80.94	1.92	74.51	28.82
32	44.40	1.76	29.33	72.23	1.48	79.54	27.91

Table 8.2.2 Lab data – Major Ion concentrations

APPENDIX B

ZONAL STATISTICS

LULC	Area (sq.km)	% of area	Acreage
Residential	3.29	3.36	21842.94
Urban	2.75	2.81	18277.27
Cropland	90.61	92.51	601248.64
Other Agriculture	0.06	0.06	369.77
Forest	-	-	-
Strip Mines	0.53	0.54	3486.41
Confined Operations	0.11	0.11	713.13
Reservoir	0.60	0.61	3961.83

Table 8.3.1 Catchment Area 1

LULC	Area (sq.km)	% of area	Acreage
Residential	1.93	1.29	47646.90
Urban	1.91	1.28	47141.85
Cropland	144.18	96.72	3562776.08
Other Agriculture	-	-	-
Forest	0.28	0.19	6951.14
Strip Mines	-	-	-
Confined Operations	0.77	0.52	19084.03
Reservoir	-	-	-

Table 8.3.2 Catchment Area 2

LULC	Area (sq.km)	% of area	Acreage
Residential	6.24	5.42	154124.35
Urban	2.00	1.73	49348.37
Cropland	100.90	87.62	2493256.32
Other Agriculture	0.30	0.26	7509.52
Forest	4.27	3.71	105580.52
Strip Mines	1.44	1.25	35580.92
Confined Operations	-	-	-
Reservoir	-	-	-

Table 8.3.3 Catchment Area 3

LULC	Area (sq.km)	% of area	Acreage
Residential	0.45	0.33	11023.52
Urban	0.12	0.09	3065.38
Cropland	135.12	98.68	3338834.28
Other Agriculture	-	-	-
Forest	0.57	0.41	14029.95
Strip Mines	0.67	0.49	16446.87
Confined Operations	-	-	-
Reservoir	-	-	-

Table 8.3.4 Catchment Area 4

LULC	Area (sq.km)	% of area	Acreage
Residential	3.76	3.90	93282.37
Urban	2.77	2.87	68599.84
Cropland	89.68	93.06	2222964.76
Other Agriculture	-	-	-
Forest	-	-	-
Strip Mines	0.11	0.11	2699.65
Confined Operations	-	-	-
Reservoir	0.05	0.05	1253.38

Table 8.3.5 Catchment Area 5

LULC	Area (sq.km)	% of area	Acreage
Residential	56.06	31.61	1385279.45
Urban	5.67	3.20	140157.65
Cropland	104.78	59.08	2589065.25
Other Agriculture	-	-	-
Forest	7.63	4.30	188483.91
Strip Mines	3.15	1.78	77801.40
Confined Operations	-	-	-
Reservoir	0.07	0.04	1812.33

Table 8.3.6 Catchment Area 6

APPENDIX C

STANDARD CALIBRATION CURVES

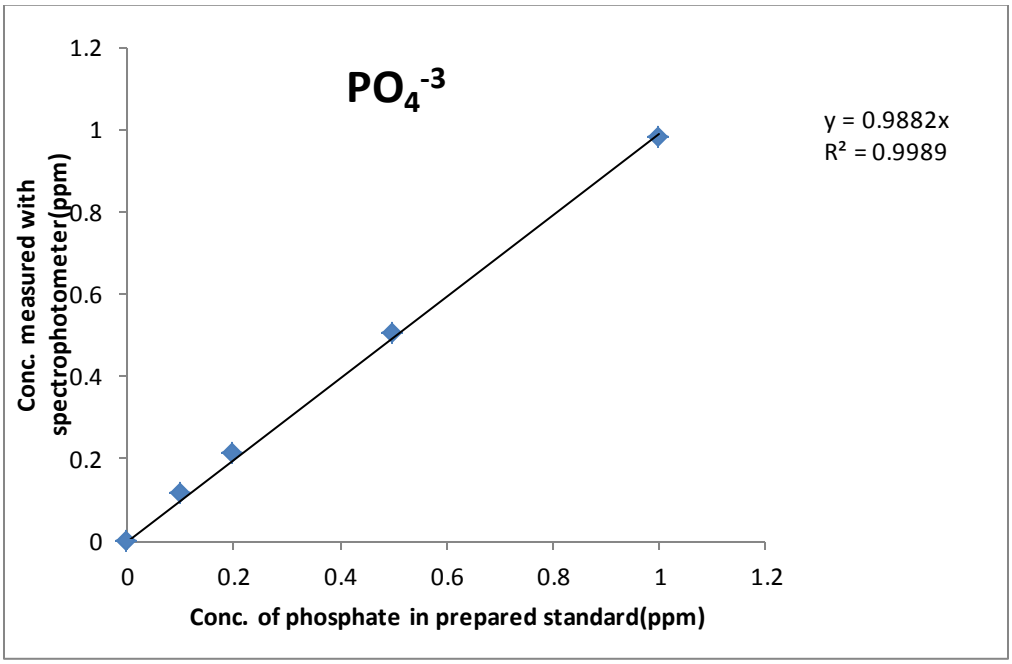

Figure 8.1 Calibration curve of Phosphate standard

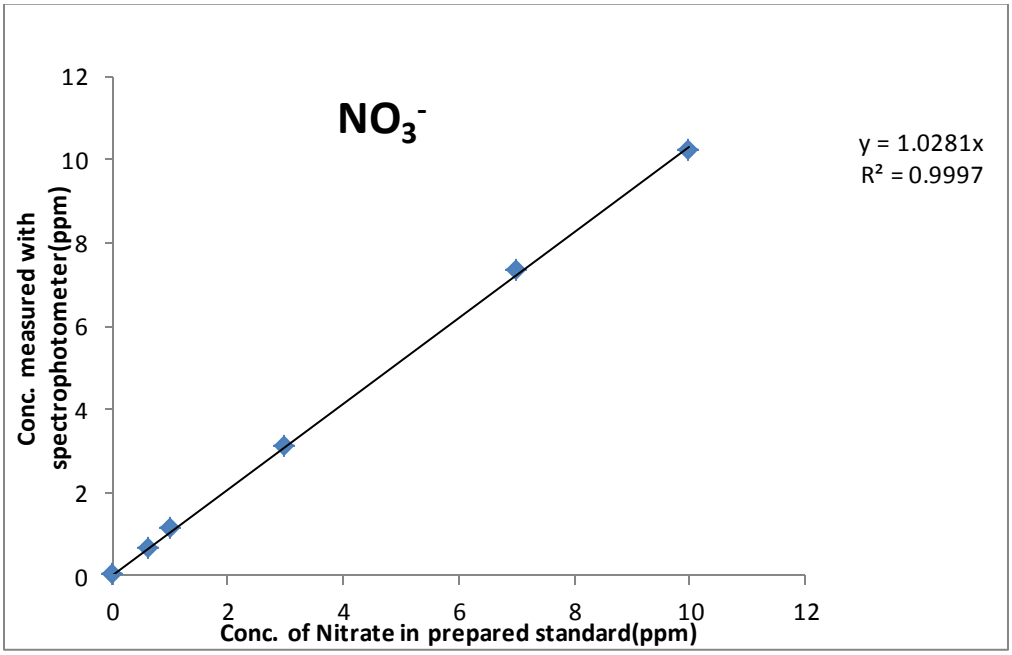

Figure 8.2 Calibration curve of nitrate standard

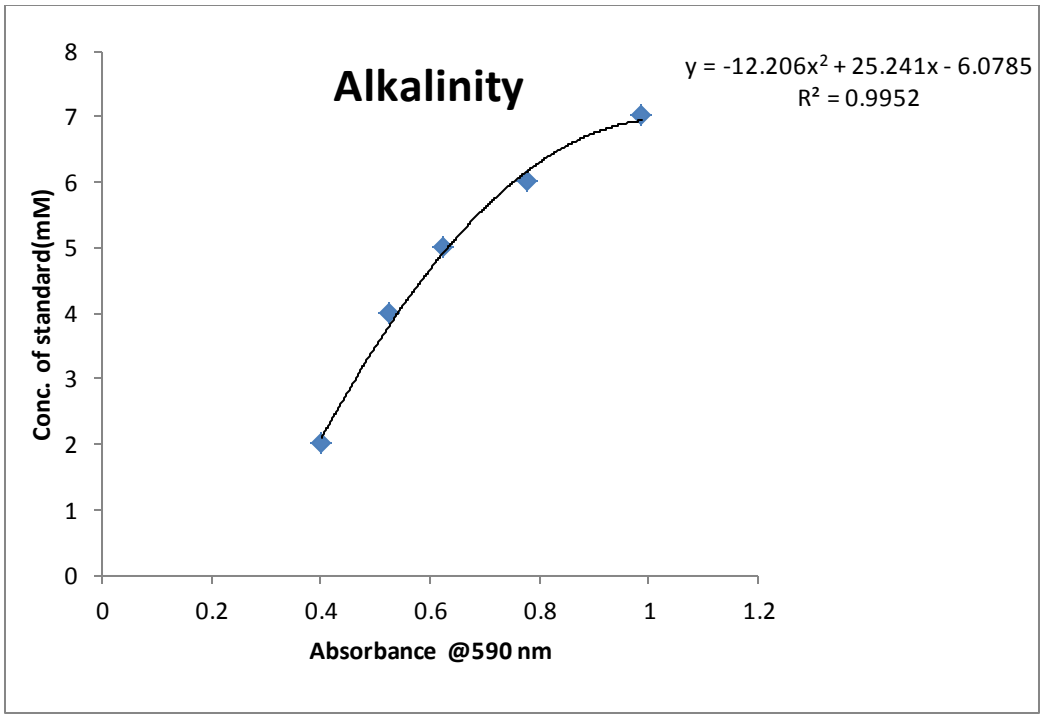

Figure 8.3 Calibration curve for alkalinity standard

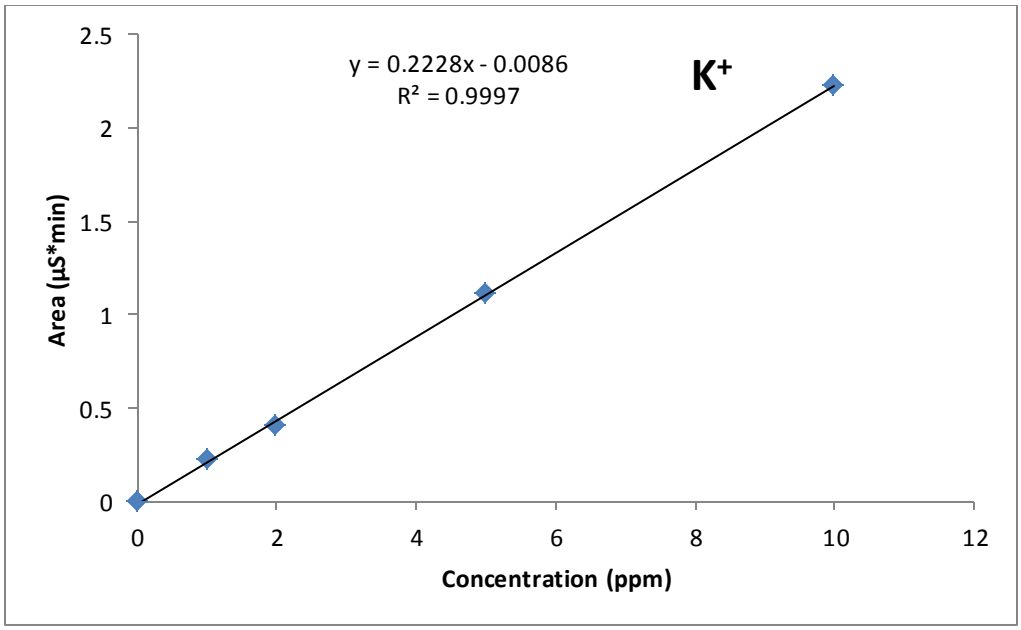

Figure 8.4 Calibration curve for Potassium standard

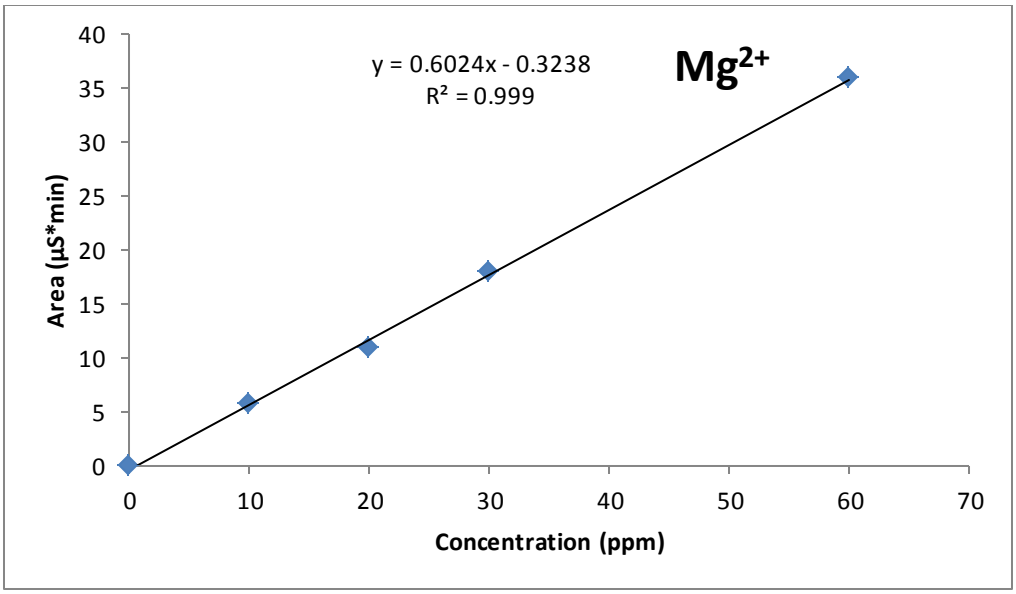

Figure 8.5 Calibration curve for magnesium standard

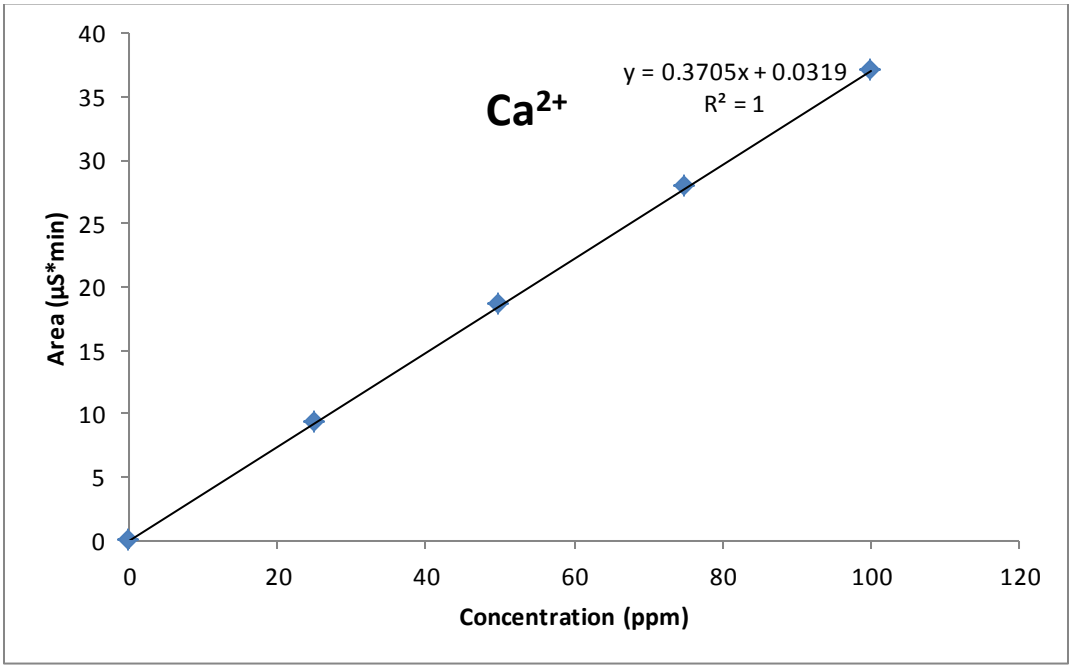

Figure 8.6 Calibration curve for calcium standard

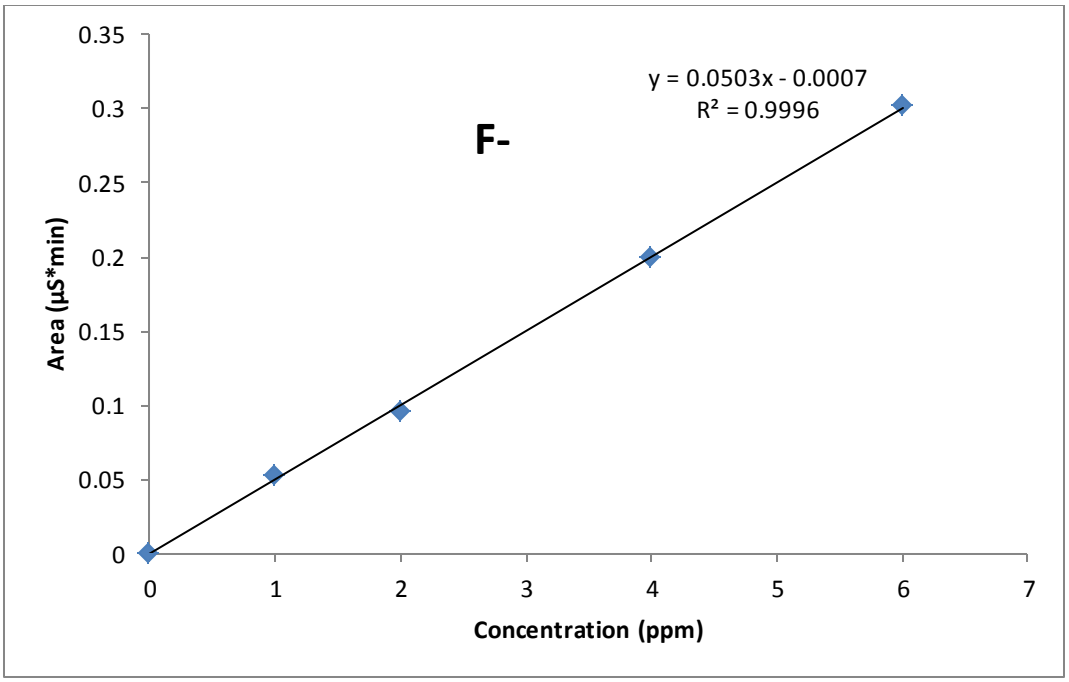

Figure 8.7 Calibration curve of Fluoride standard

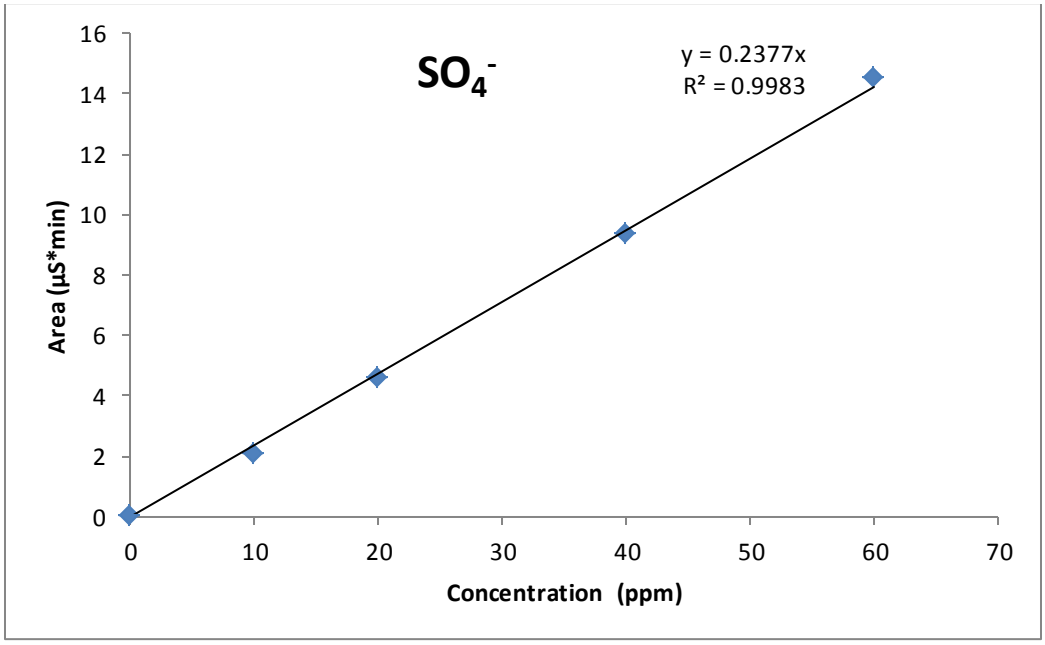

Figure 8.8 Calibration curve of sulfate standard

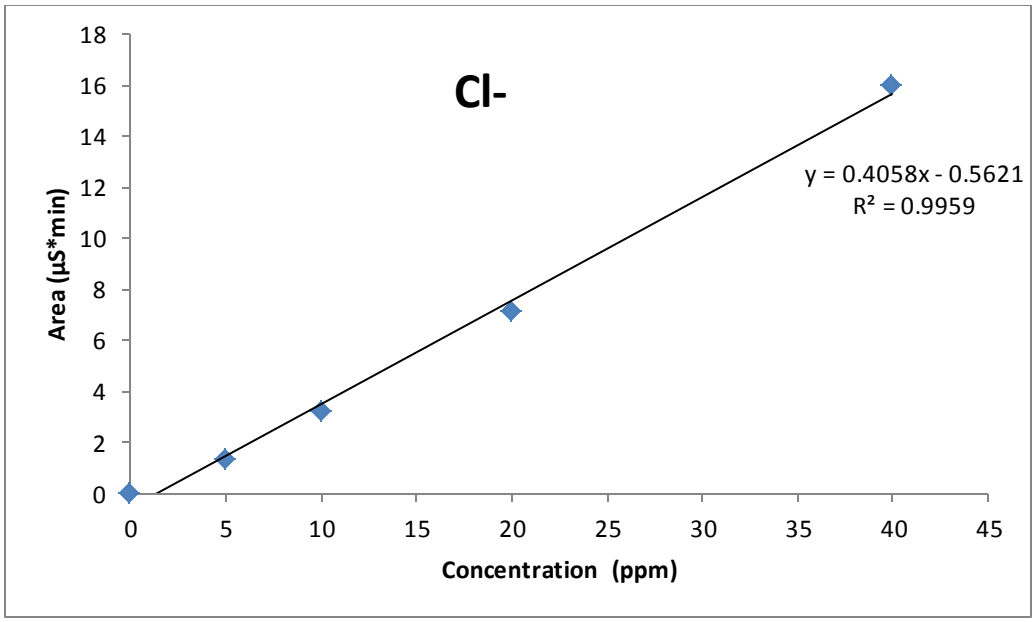

Figure 8.9 Calibration curve of chloride standard

APPENDIX D

PHREEQC Results

mple points	$\log(\alpha_{H^+})$	$\log(\alpha_{H4SiO4})$	$\log(\alpha_{Ca^{2+}})$	$\log(\alpha_{K^+})$	Saturation Index (calcite)
1	-8.1	-3.90	-3.41	-5.04	0.22
2	-8.15	-3.97	-3.25	-5.06	0.16
3	-8.27	-4.05	-3.60	-5.56	0.61
4	-8.2	-3.96	-3.26	-5.12	-0.12
5	-8.25	-4.03	-3.25	-5.06	0.30
6	-8.12	-3.96	-3.18	-4.77	0.31
7	-8.27	-4.05	-3.77	-5.23	0.03
8	-8.09	-3.89	-3.24	-5.46	0.40
9	-8.2	-3.96	-3.82	-5.34	0.65
10	-8.31	-4.07	-3.76	-5.76	0.35
11	-8.05	-3.89	-3.44	-5.06	0.58
12	-7.95	-3.83	-3.32	-4.77	0.23
13	-7.96	-3.84	-3.47	-5.12	0.20
14	-8.15	-3.95	-3.49	-5.06	0.42
15	-8.03	-3.85	-3.83	-4.77	0.30
16	-7.92	-3.83	-3.57	-5.20	0.31
17	-8.29	-4.06	-3.68	-5.04	0.27
18	-8.26	-4.04	-3.78	-5.06	0.60
19	-8.3	-4.10	-3.54	-5.52	0.70
20	-8	-3.87	-3.59	-5.51	0.22
21	-8.23	-3.98	-3.22	-5.66	0.31
22	-8.27	-4.05	-3.54	-5.06	0.47
23	-8.24	-3.96	-3.68	-4.77	0.03
24	-7.97	-3.57	-3.45	-5.33	-0.12
25	-8.16	-3.95	-3.62	-5.42	0.45
26	-8.12	-3.97	-3.78	-5.34	0.75
27	-8	-3.87	-3.27	-5.44	0.21
28	-7.96	-3.84	-3.82	-5.32	0.16
29	-7.82	-3.75	-3.77	-5.11	0.61
30	-7.88	-3.67	-3.41	-5.06	0.34
31	-7.44	-3.32	-3.47	-4.77	0.33
32	-8.18	-3.47	-3.77	-4.97	0.03

Table 8.4 Activity and Saturation Indices (calcite) data obtained from PHREEQC

APPENDIX E

PRECIPITATION DATA

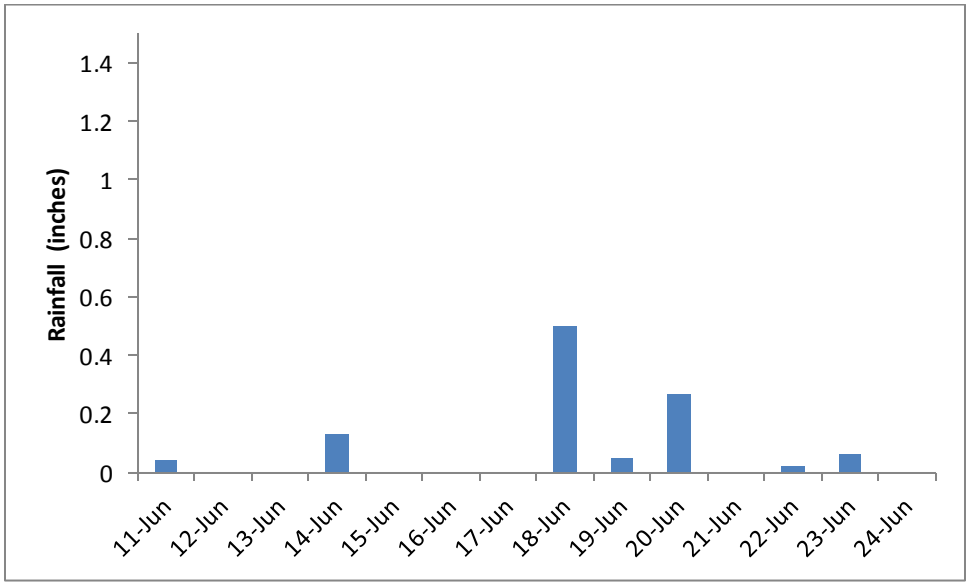

Figure 8.10 Precipitation data for Dayton region, Wilmington WS (NOAA, 2011)

APPENDIX F

SOIL MAP DOWNLOADING AND PROCESSING

Website for data downloads:

http://soildatamart.nrcs.usda.gov

Step 1: Select the state, county based on study requirement.

Step 2: Download the data from the website using your e-mail address

Step 3: In a span of 1 hr. – 1 day (approx.), download link will be e-mailed to your provided id (check inbox/ spam folder)

Step 4: WinZip file containing spatial and tabular data will be downloaded to the selected destination.

Step 5: Unzip the file to a destination folder. The unzipped file contains tabular data, spatial data and an access database template.

Step 6: open the access template and copy paste the folder link for the tabular data to be uploaded on the access database.

Step 7: Create a query in access by adding tables and select the required fields for the map

Step 8: Export the query into an excel sheet and save it as .dbf extension

Step 9: Delete the duplicate attributes by using sort on the excel sheet.

Step 10: Add the .dbf file as layer in to ArcGIS along with spatial data for the respective counties.

Step 11: Join the spatial and tabular data and further use ArcMap functionalities such as layer properties, symbology etc.

This procedure is simplified and modified from a document created by, Aaron Lantz of the Division of Soil & Water Conservation, Ohio Department of Natural Resources.